Trace Metals Pilot Project 1998
Fall Creek Watershed Study Report

Federal Grant CP 985282-01

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ABSTRACT

The National or State Water Quality Criteria (WQC) for metals are primarily based on acid-soluble portion of the metals, but the water quality based effluent limits for metals as required by USEPA {**40 CFR 122.45 (c)** }and defined in **40 CFR Part 136** are always expressed as total recoverable metals. More recently, for inside the Great Lakes Basin, Indiana has adopted WQC for metals that are expressed in terms of the dissolved fraction of the metal, but even in this instance water quality based effluent limits for metals ought to be expressed as total recoverable metals.

Recently, EPA has demonstrated that using the **Clean Sampling Techniques** and **Low Detect Ultra-Clean Analytical Test Methods** for sampling and analysis for metals have resulted in metal concentrations in effluent and ambient waters in lower numbers than those previously obtained by using conventional methods for sampling and EPA recommended conventional analytical test methods. Consequently, a **Trace Metal Pilot Project** was proposed by IDEM to develop in-house expertise in sampling ambient waters using **1996 USEPA Method 1669** or "**Clean Sampling Techniques**" and analyze the ambient water samples for dissolved and total recoverable metals using the **Low Detect Ultra-Clean Analytical Test Methods**. The necessary funding for this pilot project was obtained through a **Federal Grant CP 985282-01, USEPA Section 104 (b) (3**). The **Wisconsin State Laboratory of Hygiene** (**WSLH**) at the University of Wisconsin, Madison, WI., was contracted by IDEM to provide training and expertise in Clean Sampling Techniques and to provide all the services to analyze water samples for dissolved and total metals by low detect **Inductively Coupled Plasma-Mass Spectrometry** (**ICP/MS**), and several other parameters by conventional analytical test methods.

Fall Creek, a point and non-point source targeted Watershed within the **White River Basin** located within close proximity to IDEM in Indianapolis, was selected as the primary site for this Trace Metal Pilot Project. In this watershed, Fall Creek is dammed to form an eight miles long **Geist Reservoir**, one of Indianapolis's public water supplies. A total of five Sampling locations were chosen in this watershed, one location each from Upstream and Downstream of the Geist Reservoir and three sampling locations from Upper, Middle and Lower part of the Geist Reservoir. Four sampling events were planned and completed in the month of **May, July, August** and **September 1998**. In each sampling event, water samples were collected from five sampling locations in the Fall Creek by using the Clean Sampling Techniques.

A total of **20 Metals**, **11 Non-metals** and **5 Hydrolab parameters** were analyzed for this pilot project at the WSLH and/or in the field. With the exception of Calcium, Potassium, Magnesium, and Sodium that were analyzed just for dissolved metals, all other metals were analyzed for both dissolved and total recoverable metals.

Except for the **Silver metal**, all 19 metals were detected in the ambient water. In any of the sampling events **Silver** metal was not detected either as dissolved or total metal (**Limit of Quantitation 0.03 ug/L**) at any of the sampling location in Fall Creek

Among the several metals, ten metals (**Aluminum, Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Selenium** and **Zinc**) were most conspicuous and were detected as both dissolved and total recoverable metals at all the five sampling locations in the Fall Creek. Except for **Aluminum**, no other metal was present in any significant amounts. Again among the ten conspicuous metals in the Fall Creek, five metals (**Aluminum, Lead, Mercury and Zinc**) were mostly present as total recoverable metals and the dissolved metal concentrations for the same metals were very low.

Except for the **Total Aluminum**, concentrations for any of the metal did not exceed the aquatic life chronic water quality criteria for dissolved or total metals calculated at **250 mg/L median hardness of Fall Creek**. The exact source and reason for high concentrations of Total Aluminum in Fall Creek is not known. It is speculated that the most likely origin and source for this metal could be the natural crust in the Fall Creek.

The total metal concentrations for many metals (**Cadmium, Chromium, Copper, Lead, Mercury, Nickel** and **Zinc**) found in this study from Fall Creek were 5 to10 times lower than the total metal concentrations found previously from a **Fixed Station Site** (**FC 0.6**) which is located downstream of the 5th Sampling Location in the Fall Creek. The differences found in the total metal concentrations between this and the previous study could be due to several reasons, and the one most conspicuous reason could be the Clean Techniques used for both sampling and analyses in this pilot study as compared to in the earlier studies where conventional methods were used for both sampling and analyses.

The **1996 USEPA Method 1669**, or "**Clean Sampling Technique**" is primarily developed to support the implementation of water quality at EPA water quality criteria levels. This method is especially suitable for sampling and analyzing ambient waters for metals (**Antimony, Cadmium, Copper, Lead, Mercury, Nickel, Silver, Thallium** and **Zinc**) for which WQC are below the detection limits by the conventional analytical test methods. The Clean Sampling Technique works very well with the **Low Detect Ultra-Clean Analytical Test Methods** and usually provides metals data at lower concentrations than the one obtained by using the conventional methods for sampling and EPA recommended conventional test methods for analyses. However, Clean Sampling Techniques is very slow and labor intensive and may not be feasible for routine and large scale sampling and analysis of ambient waters for monitoring the water quality. In lieu of this, conventional methods for sampling of ambient waters and the use of **Low Detect Ultra-Clean Test Method** such as **ICP/MS** could be a good substitute to analyze ambient waters to monitor water quality for metals for which the WQC are below the detection limits by conventional **Graphite Furnace, Atomic Absorption** or **Inductively Coupled Plasma** (**ICP**) test methods.

INTRODUCTION

Background

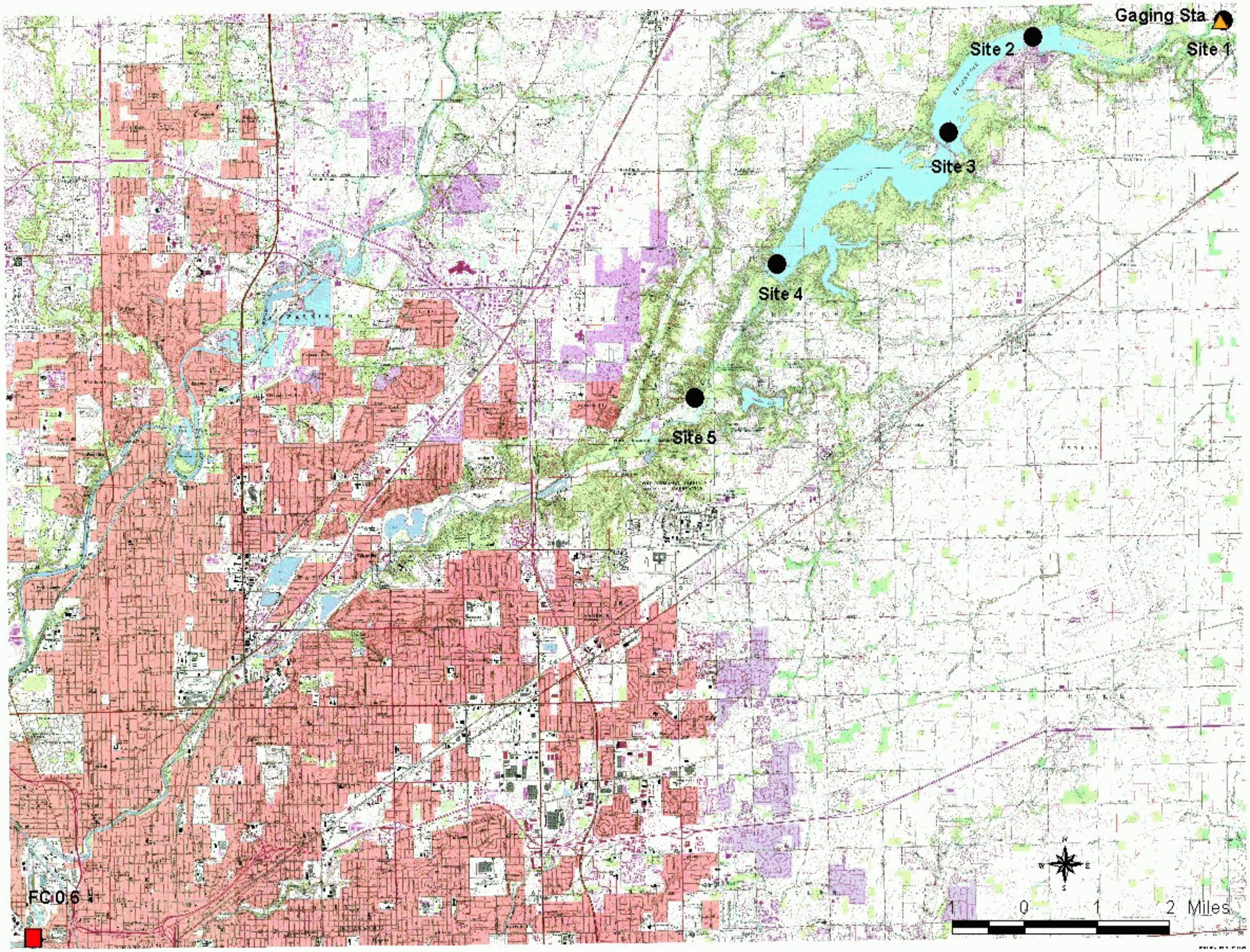
Expertise in "**Clean Sampling Techniques**" of surface water is needed to be developed within IDEM in order to collect and analyze low level dissolved trace metals in surface water samples, to provide enhanced monitoring of **Priority Toxic Pollutant Metals,** for watershed pollution control from point and non-point source discharges. In February 1997, in addition to regular **Water Quality Criteria** (**WQC**) for toxic metals, Indiana under the **Great Lakes Initiative** (**GLI**) has adopted WQC that are based on concentrations of dissolved metals for watersheds in the Great Lakes Basin. Therefore, results of low level dissolved trace metals, especially in the Great Lakes Basin, are required to assess the waters for compliance with the new WQC. In the rules applicable outside the Great Lakes and adopted by Indiana in 1990, the WQC are not expressed in the dissolved form, however, the rules do allow for the WQC to be adjusted to take into account the difference between the soluble and total recoverable form of a metal.

Recently, USEPA has demonstrated that "Clean Sampling Techniques" and Low Detect "Ultra-Clean" analyses for metals have resulted in values significantly different from those obtained with the conventional techniques currently employed by IDEM and other states. Therefore, this project, funded through a **Federal Grant CP 985282-01**, **USEPA Section 104(b)(3)**, was designed (see **Appendix A**, **Scope of Work**) to provide IDEM with the opportunity to develop sampling techniques for acquiring and analyzing ambient water samples for **dissolved** and **total recoverable metals** at trace levels (**nanogram/liter**) for comparison with Water Quality Standards (WQS) that are based on low level dissolved or total recoverable metals. The **Wisconsin State Laboratory of Hygiene (WSLH)** at the University of Wisconsin, Madison, Wisconsin, was selected as the Contract Laboratory by IDEM to provide training for sampling surface water using "**Clean Sampling Techniques**" and also to analyze the water samples using **Low Detect Ultra-Clean Analytical Methods**. A **Trace Metal Quality Assurance Project Plan** (**QAPP**) was prepared exclusively for this pilot project which described procedures and quality control requirements for sampling and analyses. This report is written to fulfill the final requirement to compile, analyze and interpret the data collected for this project.

Site Description

Fall Creek, a non-point and point source priority targeted watershed within the **White River Basin**, was selected as the representative site for the Trace Metals Pilot Project. The selected study area of Fall Creek Watershed is about 10 miles away from IDEM and geographically is in the Northeast part of the City Indianapolis. In this watershed, **Fall Creek** is dammed to form an eight miles long **Geist Reservoir,** one of Indianapolis Public Water Supplies. This Watershed covers areas in four major Counties (**Madison, Hancock, Hamilton and Marion**). The Fall Creek Watershed and the **five (5) sampling locations** selected for this pilot project are shown on the attached map **(Figure 1).** Some of the reasons and advantages for selecting this Watershed as a site for this pilot project are:

FIGURE 1. Fall Creek Watershed and Sampling Locations



- The upper portion of the **Fall Creek Watershed** drains agricultural land while lower Fall Creek runs through an urban environment with combined sewer out falls. The Fall Creek is a sub-watershed of the White River Basin and was assessed as one of the watersheds for the OWM water quality monitoring strategy during 1996-1997 (extra work in 2nd year was not completed.

- The selected five sampling locations, **two (2) in the Fall Creek (one Upstream and one Downstream)** and **three (3) sampling locations from Upper, Middle, and Lower part of the Geist Reservoir**, provide an opportunity to collect water samples from a boat in the Geist Reservoir and to collect wading samples from the Fall Creek. In addition, these sampling locations will provide first hand experience in "**Clean Sampling Techniques**" for sampling surface water from a flowing stream and from a reservoir or a lake using a grab sample or sample pumping system (peristaltic pump), and subsurface sampling devices where depth profiling is also important.

- Limited total recoverable metals data detected by using conventional sampling and analytical techniques from Fall Creek Fixed Station Site (FC 0.6) are available for comparison with the results obtained in this study using clean sampling techniques for filterable dissolved and total recoverable metals. Information gathered in this study, as part of the on going Assessment Branch Water Quality Monitoring Program, will also be used to assess the overall quality of the surface water in the Fall Creek Watershed for compliance with the WQS for several toxic metals.

Project Data Quality Objectives

The **Project Data Quality Objectives** (**PDQOs**) are qualitative and quantitative statements which describe specific objectives of the project in terms of major tasks or phases of the proposed work. The seven main PDQOs and major tasks set for this **Trace Metals Pilot Project** were:

1. Establish "**Clean Sampling Techniques**" and expertise within IDEM by collecting ambient water samples for analysis at a Contract Laboratory for dissolved and total recoverable metals. The USEPA **"Sampling Method 1669"** will be used by IDEM staff to collect water samples for this purpose. Newly developed **ICP/MS** (**Inductively Coupled Plasma-Mass Spectrometry**) **Test Method 1638** applicable to Sampling Method 1669 for laboratory analysis of several metals at nanogram levels; **Standard Method 3120B** for analysis of Iron, Calcium, Magnesium, Sodium and Potassium. EPA **Test Method 1632** applicable to Sampling Method 1669 will be used for analysis of Mercury

2. Evaluation of laboratory analytical metal data for the presence of not only total recoverable metals but also dissolved metals in surface water which otherwise would have been quantified as below detection levels by the conventional analytical test methods (**Atomic Absorption Graphite Furnace or Inductively Coupled Plasma (ICP) Procedure**).

3. Analytical metals data gathered from this pilot project will help determine the presence of actual amounts of dissolved and total recoverable metals in a particular water body or a watershed. This information with respect to the individual metal parameter will be vital and would be useful to compare for compliance with the existing and new WQC, and for use as the background concentration for setting the **Waste Load Allocation** (**WLA**) with respect to dissolved or total recoverable metal concentrations for issuance of a NPDES permit.

4. This Pilot project has been designed to provide IDEM staff with an opportunity to develop expertise in "**Clean Sampling Techniques**" using "**Clean Hands**" and "**Dirty Hands**" for future water quality monitoring studies across the State. **Fall Creek Watershed** for several reasons and advantages was chosen for this pilot study A complete description of the selected site, with geographical boundaries and areas covered for this pilot study is described on earlier pages (see **Site Description** on Page 1 and **Figure 1** on Page 2). The "Clean Sampling Techniques" are further discussed in **Section 6** "**Sampling Procedures**" of the **1998 Quality Assurance Project Plan (QAPP) for the Trace Metal Pilot-Project** and in **Materials & Methods** of this report. The actual sampling and analysis for this project started in May 1998 and ended on September 30, 1998 when the EPA grant for this project terminated.

5. Information gathered from this pilot project will be useful in extending this work in the future to other Major River Basins or other Watersheds in Indiana as part of the on-going **Fixed Station Monitoring Program**, **development of Total Maximum Daily Loads** (TMDLs) works and other **Water Quality Monitoring Programs** at IDEM. Future works under these programs will generate data with respect to total and dissolved metal concentrations in surface water, their comparison with the WQC for metals and their use as background concentrations for setting WLAs for issuance of NPDES permits applicable to total recoverable or dissolved metal water quality criteria.

6. Possibilities exist that errors could be made while sampling surface water using "**Clean Sampling Techniques**". Contamination of water samples may occur while collecting, filtering and transferring water samples to sampling bottles or as a result of contamination of sampling bottles and other equipment used in surface water sampling. To assure that our sampling techniques and preparations are 'in control', quality controls according to the Trace Metal QAPP were followed. Errors of these kind could produce test results of metals data that would need to be discarded and would require revisiting the site for resampling and reanalysis of the water samples, if necessary.

7. This Pilot project was designed to accomplish and achieve all the above project objectives and to provide IDEM staff involved in sampling surface water with first hand experience and expertise in "**Clean Sampling Techniques**" of surface water, and its analysis using low detect **Ultra Clean Analytical Test Methods at a Contract lab (WSLH)**. One of the expected product coming out of this pilot project would be the development of a **Standard Operating Procedure** (**SOP**) on **"Clean Sampling Techniques"** for sampling surface water for future use by IDEM staff.

MATERIALS AND METHODS

Materials:

a. Equipment and Supplies:

The **Wisconsin State Laboratory of Hygiene** (**WSLH**) at the University of Wisconsin, Madison, Wisconsin was retained by IDEM as the Analytical Contract Lab. The lab supplied to IDEM a majority of the equipment and laboratory supplies for the Trace Metal Pilot Project. For example, the WSLH provided to IDEM clean sampling bottles, ultra-pure preservatives, ultra-pure deionized water, filters, peristaltic pump, other necessary equipment and supplies for collection and filtration of water samples in the field, and shipping containers.

Some of the essential apparatus, equipment, laboratory supplies and services provided to IDEM by WSLH are listed in **Table 1**.

TABLE 1
Sampling Apparatus: Equipment and Preservatives

Sampling Apparatus	Description
Bottles	Fluropolymer bottles were used for trace metals. Polyethylene or Polycarbonate bottles were used for other parameters.
Cleaning	Detergent wash and rinse in ultra-pure-pure Demonized water (DI). Soak overnight in 50% HCl and rinse with ultra-pure DI water. Soak overnight in hot (70°) 50% HNO_3 and rinse with ultra-pure DI water. Fill mercury bottles with 0.5% ultra-pure HCl and other metals bottles with 2% HNO_3, bag and store in clean lab. Before shipping, drain, rinse with ultra-pure DI water and dry. Add 10 ml of 0.5% ultra-pure HCl to mercury bottles and double bag all bottles. All cleaning and bagging procedures were performed at the WSLH Contract lab.
Gloves	Powder free (non-talc) latex, polyethylene or polyvinyl chloride.
Filter	**Meisner Alpha** capsule filter equipped with 0.45 um filter with a minimum 1000 cm^2 filtration area. Filters were cleaned by soaking for 2 days in 20% HCl, rinsed with ultra-pure DI water, soaked for 4 days in 20% HNO_3, rinsed with ultra-pure DI water and double bagged. (5 ml/500 ml water sample). For the suspended particulate, a separate set of clean preweighed filters were supplied by WSLH Contact lab.
Preservative	Water samples for Mercury were preserved in the field with 50% ultra-pure HCL (5 ml/500 ml water sample), while the water samples for other metals are preserved with 50% HNO (10 ml/250 ml water sample)$_3$ with pH lowered to < 2. Water samples for hexavalent chromium were preserved with 25% NaOH (2 ml/125 ml water samples). All water samples were preserved at the site immediately after sample collection and placed in ice filled cooler.

In addition to the above, numerous equipment and supplies were utilized for collecting water samples from land or a boat using clean sampling techniques.

A complete listing of all the other necessary equipment, supplies and apparatus that were needed and used for this pilot project is provided below.

Clean Sampling Gear:

Geo-pump (Peristaltic Pump)
Geo-Pump Battery
Plastic tubs containing supplies.
Plastic bow boom

Basic Boat Gear:

Fiberglass Boat (Boston Whaler)
Plastic-coated anchor with 70-ft line
Electric trolling motor
Trolling motor battery
Oars
Depth finder
Life Jackets

Supplies:

For In-Boat Sampling:

Clean suits (optional)
Wrist and shoulder gloves
Plastic bags
Kevlar support line
Fiberglass boom cleat adaptor
Bungee cord
Teflon sampling line
Teflon sampling line weight
Teflon tubing
Teflon adaptor fittings
Poly-wash bottle with dilute acid and MQ-water
Zip-lock bags
1000 ml graduated cylinder
Sampling platform
Canopy bags, wipers
Teflon Container (10 L) for dilute acid waste
Teflon Container (4 L for dilute acid rinse

For On-Land Sampling:

Clean suits (optional)
Wrist and shoulder gloves
Plastic bags
Teflon sampling line
Teflon sampling line weight
Teflon tubing
Teflon adaptor fittings
Poly-wash bottle with dilute acid and MQ-water
Zip-lock bags
Graduated cylinder (1000 ml)
Sampling platform
Canopy for ground
Canopy bags, wipers
Teflon Container (10 L) for dilute acid waste
Teflon Container (4 L) for dilute acid rinse

Field Blank Kit:

1 Teflon bottle (5000 ml) filled with Milli-Q water.
1 Teflon bottle (3000) filled with Milli-Q water.
3 Teflon bottles for trace metal samples.
3 Teflon bottles (500 ml) for mercury samples.

Short lengths (2 ft) of Teflon Tubing.
Filter Capsule (Meisner filters, several)
C-Flex Tubing.
Teflon Cap with hole for 3 and 5L bottles.
Teflon Cap with hole for 3 and 5L bottles.
Zip-lock bags for 5L bottle caps
Plastic bags

b. Target Parameters:

Target physical and chemical parameters selected for the Trace Metals Pilot Project, **Method Detection Limit (MDL)** and **Limit Of Quantitation (LOQ)** plus the expected Precision and Accuracy for the individual parameter are listed in **Table 2 (Pages 8-10)**. The majority of the selected metal parameters are those for which WQS already exist and/or on the EPA Clean Water Act (CWA) Section 307 (a) "**Toxic Priority Pollutants List**".

The breakdown of Parameters selected for this project was as follows:

- 20 Metals (38 including both total & dissolved Cr III & Cr VI)
- 11 Non-metals and
- 5 Hydro Lab parameters (see **Table 2**).

TABLE 2
Target Parameters, Method Detection,Quantitation Limits, and Expected Precision and Accuracy

PARAMETER	CAS Number	Analytical Method	Test Method	Method Detection Limit (µg/ ℓ)	Limit Of Quantitation (µg/ ℓ)	Precision QC limit (% RPD)	Accuracy Matrix Spike (% Recovery)
METAL PARAMETERS							
Antimony, dissolved	7440-36-0	ICP/MS	EPA 1638	0.01	0.03	± 15	100 ± 15
Antimony, total recoverable	7440-36-0	ICP/MS	EPA 1638	0.01	0.03	± 15	100 ± 15
Arsenic, dissolved	7440-38-2	ICP/MS	EPA 1638	0.1	0.4	± 15	100 ± 15
Arsenic, total recoverable	7440-38-2	ICP/MS	EPA 1638	0.1	0.4	± 15	100 ± 15
Beryllium, dissolved	7440-41-7	ICP/MS	EPA 1638	0.01	0.04	± 15	100 ± 15
Beryllium, total recoverable	7440-41-7	ICP/MS	EPA 1638	0.01	0.04	± 15	100 ± 15
Cadmium, dissolved	7440-43-9	ICP/MS	EPA 1638	0.01	0.03	± 15	100 ± 15
Cadmium, total recoverable	7440-43-9	ICP/MS	EPA 1638	0.01	0.03	± 15	100 ± 15
Chromium, dissolved	7440-47-3	ICP/MS	EPA 1638	0.02	0.06	± 15	100 ± 15
Chromium,, total recoverable	7440-47-3	ICP/MS	EPA 1638	0.5	1. 5	± 15	100 ± 15
Chromium - III *	16065831	ICP/MS/Ion chromatography	EPA 1638	0.5	1. 5	+ 15	100 +15
Chromium - VI, dissolved	18540299	Ion chromatography	EPA 1636	0.5	1. 5	+ 15	100 +15
Copper, dissolved	7440-50-8	ICP/MS	EPA 1638	0.01	0.04	± 15	100 ± 15
Copper, total recoverable	7440-50-8	ICP/MS	EPA 1638	0.01	0.04	± 15	100 ± 15
Lead, dissolved	7439-92-1	ICP/MS	EPA 1638	0.005	0.02	± 15	100 ± 15
Lead, total recoverable	7439-92-1	ICP/MS	EPA 1638	0.005	0.02	± 15	100 ± 15
Manganese, dissolved	7439-96-5	ICP/MS	EPA 1638	0.01	0.03	± 15	100 ± 15
Manganese, total recoverable	7439-96-5	ICP/MS	EPA 1638	0.01	0.03	± 15	100 ± 15
Mercury, dissolved	7439-97-6	CVAFS	EPA 1631	0.0001	0.0003	± 15	100 ± 15
Mercury, total recoverable	7439-97-6	CVAFS	EPA 1631	0.0001	0.0003	± 15	100 ± 15
Nickel, dissolved	7440-02-0	ICP/MS	EPA 1638	0.09	0.3	± 15	100 ± 15
Nickel, total recoverable	7440-02-0	ICP/MS	EPA 1638	0.09	0.3	± 15	100 ± 15
Selenium, dissolved	7782-49-2	ICP/MS	EPA 1638	0.3	1	± 15	100 ± 25
Selenium, total recoverable	7782-49-2	ICP/MS	EPA 1638	0.3	1	± 15	100 ± 25
Silver, dissolved	7440-22-4	ICP/MS	EPA 1638	0.009	0.03	± 15	100 ± 15
Silver, total recoverable	7440-22-4	ICP/MS	EPA 1638	0.009	0.03	± 15	100 ± 15

PARAMETER	CAS Number	Analytical Method	Test Method	Method Detection Limit (μg/ ℓ)	Limit Of Quantitation (μg/ ℓ)	Precision QC limit (% RPD)	Accuracy Matrix Spike (% Recovery)
Thallium, dissolved	7440-28-0	ICP/MS	EPA 1638	0.004	0.012	± 15	100 ± 15
Thallium, total recoverable	7440-28-0	ICP/MS	EPA 1638	0.004	0.012	± 15	100 ± 15
Zinc, dissolved	7440-66-6	ICP/MS	EPA 1638	0.04	0.15	± 15	100 ± 15
Zinc, total recoverable	7440-66-6	ICP/MS	EPA 1638	0.04	0.15	± 15	100 ± 15
Aluminum, dissolved	7429-90-5	ICP/MS	EPA 1638	0.1	0.3	± 15	100 ± 15
Aluminum, total recoverable	7429-90-5	ICP/MS	EPA 1638	0.1	0.3	± 15	100 ± 15
Iron, dissolved	7439-89-6	ICP	SM 3120B	0.003 mg/l	0.008 mg/l	± 10	100 ± 14
Iron, total recoverable	7439-89-6	ICP	SM 3120B	0.003 mg/l	0.008 mg/l	± 10	100 ± 14
Calcium, dissolved	7440-70-2	ICP	SM 3120B	6	20	± 10	105 ± 12
Magnesium, dissolved	7439-95-4	ICP	SM 3120B	10	40	± 10	104 ± 14
Potassium, dissolved	7440-09-7	AAS Flame	SM 3111B	20	60	± 10	100 ± 15
Sodium, dissolved	7440-23-5	ICP	SM 3120B	10	30	± 10	103 ± 17
NON-METAL PARAMETERS							
Alkalinity, dissolved	E-14506	Titration	EPA 310.1	1 mg/ ℓ	3 mg/ ℓ	± 2	N/A
Chloride, dissolved	16887006	Ion chromatography	EPA 300.0	0.02 mg/ ℓ	0.08 mg/ ℓ	± 10	100 ± 15
Hardness (as $CaCO_3$)	E-11778	Ca + Mg	SM 2340	0.1 mg/ ℓ	0.4 mg/ ℓ	± 10	N/A
Nitrogen, nitrate, dissolved	14797558	Ion chromatography	EPA 300.0	0.003 mg/ ℓ	0.01 mg/ ℓ	± 15	100 ± 15
Nitrogen, total (TKN), dissolved	E-10264	Autoanalyzer	JWPCF[1] [1]	0.2 mg/ ℓ	1 mg/ ℓ	± 15	100 ± 25
Phosphorus, dissolved	7723140	Lachat analyzer	SM 4500P-F	0.002 mg/ ℓ	0.006 mg/ ℓ	± 15	100 ± 15
Suspended particulate matter (SPM)	-	Gravimetric	S&P IV 2.1[2]	0.08	0..27 mg/l	± 15	100 ± 15
Solids, filterable residue (TDS)	E-10173	Gravimetric	SM 2540C	7 mg/l	28.6 mg/l	± 10	N/A
Solids, total residue (TS)	E-10151	Gravimetric	SM 2540B	7 mg/l	28.6 mg/l	± 10	N/A
Sulfate , dissolved	14808798	Ion chromatography	EPA 300.0	0.01 mg/ ℓ	0.05 mg/ ℓ	± 15	100 ± 15
Organic carbon, dissolved (DOC)	-	TOC analyzer	SM5310 B	0.3 mg/ ℓ [3]	1 mg/ ℓ [3]	± 11	100 ± 20

[1] Bowman and Delfino, 1982. Determination of total kjeldahl nitrogen and total phosphorus in surface and wastewater; *Journal Water Pollution Control Federation*, 54,1324.

[2] Strickland and Parsons, 1968. A Practical Handbook for Seawater Analysis, Queen’s Press, Ottawa, Canada.

[3] Estimated; SM = Standard Methods, 19th Edition, 1995

PARAMETER	CAS Number	Analytical Method	Test Method	Method Detection Limit (µg/ ℓ)	Limit Of Quantitation (µg/ ℓ)	Precision QC limit (% RPD)	Accuracy Matrix Spike (% Recovery)
HYDROLAB PARAMETERS							
Dissolved oxygen (DO)	E-14539	Hydrolab	SM 4500-O	0.01 mg/l	0.03 mg/l	± 20	N/A
Turbidity	N/A	Hydrolab	SM 2130	0.1 NTU	0.3 NTU	± 20	N/A
Specific Conductance	N/A	Hydrolab	SM 2510	1 umhos/cm	3 umhos/cm	± 20	N/A
pH	N/A	Hydrolab	SM 4500-H	0.01 SU	0.03 SU	± 20	N/A
Water temperature	N/A	Hydrolab	SM 2550	0 ^{o}C	-5 ^{o}C	± 20	N/A

* Chromium- III by difference between total chromium and hexavalent chromium.
NTU = Nephelometric Turbidity Units: umhs = Micro ohms/cm; SU = Standard Units

Note; Instead of Arsenic III and Arsenic V listed in the **Scope of Work** (**see Appendix A**), Arsenic, as Dissolved and Total Recoverable metal will be measured. In addition, the List of Target Parameters in **Table 2** has been expanded to include Antimony, Beryllium, Thallium (both Dissolved & Total Recoverable Metals) and a few other associated parameters not listed previously in the **Scope of Work** (**Appendix A**).

Methods:

a. Sampling Location and Rationale:

In February 1997, Indiana under the Great Lakes Initiative, adopted Water Quality Standards (WQS) that are based on concentrations of dissolved metals for watersheds in the Great Lakes Basin. Therefore, low level measurements of dissolved metals are required to assess the waters for compliance with the new WQS. This also necessitated the use of “Clean Sampling Techniques” not previously utilized by IDEM. As a result, a Trace Metal Pilot Project was proposed (see **Appendix A**, **Scope of Work**) and the necessary funding for this project was obtained by a Federal Grant to provide IDEM with the opportunity to develop “Clean Sampling Techniques” for acquiring and analyzing water samples for Dissolved and Total recoverable metals at trace levels (nanogram/liter) in ambient waters.

For the Trace Metal Pilot Project, **Fall Creek**, a non-point source and point source targeted Watershed within the **White River Basin** was selected (see **Figure 1**). The selected study area of Fall Creek Watershed is about 10 miles away from IDEM and geographically is in the Northeast part of the City Indianapolis. In this watershed, Fall Creek is dammed to form the **Geist Reservoir**, one of Indianapolis’s public water supplies. This site was selected due to its importance to a large community, its close proximity to IDEM and its physical variation between the sampling locations.

Surface water samples were collected from the Fall Creek Watershed from five different locations (one sampling location each from upstream and downstream of the Geist Reservoir, and three sampling locations from upper, middle and lower part of the Geist Reservoir). Each location was subsequently sampled for surface water in four separate sampling events, using **Clean Sampling Techniques** and sensitive low detect analytical methods to gather dissolved and total recoverable metal data. Each of the four sampling events and their corresponding dates were as follows:

Sampling Event	Sampling Dates
1	May 4 and 5, 1998
2	July 15, 16, 21, and 23, 1998
3	August 10, 11, and 12, 1998
4	September 8, 9, and 10, 1998

b. Sampling Procedures:

The 1996 USEPA Sampling **“Method 1669"** was followed during the collection of water samples for laboratory analysis of dissolved and total recoverable metals. This method described the “**Clean Sampling Techniques”** for both sample collection and filtration process that are necessary to minimize contamination. Initial training for sampling of ambient waters using “**Clean Sampling Techniques**” was provided to IDEM staff by the WSLH, a Contractor Laboratory retained by IDEM.

Ambient or surface water samples were collected using one or more **Grab** sample collection techniques**.** These techniques included procedures for collecting surface water samples either using a grab sampling device or directly pumping the surface water into a sample bottle through a Teflon line or tubing with a peristaltic pump, described in the **USEPA Sampling Method 1669**.

Collection of water samples using Clean Sampling Techniques was labor intensive and required several precautions and procedures. The complete listing of various precautions and procedures used for this clean sampling project is shown below.

i. Precaution Measures for Clean Sampling

- Use “**Clean Hands Dirty Hands**” techniques.
- Use fiberglass boat.
- Use clean sampling and filtration apparatus.
- Use ultra-pure acids for samples preservation.
- Double bag sample bottles before and after sampling.
- Collect ambient water samples from sites that are several hundred feet from any metal supports or structures.
- Minimize exposure during sampling operations of sample to human, atmospheric, and other sources of contamination.
- Put on clean gloves at sampling site before beginning sample collection.

ii. Sampling Set-Up

<u>For Land-Sampling</u>:

- Lay clean tarp on a level portion of ground as close to water as possible
.
- Put together plastic round table and set table and supply storage containers (plastic tubs) on the clean tarp.
- Put battery for pump under table for easy access.
- Put plexiglass platform, supplied by WSLH, onto the table.
- Set pump inside the platform and connect pump to battery with cables.
- Insert canopy frame, covered with a large clear plastic bag, onto the platform.
- Position tubs containing supplies and other sampling equipment in appropriate positions (easily accessible) on the tarp.

<u>For Boat-Sampling:</u>

! Hook the plexiglass sampling platform over the gunnels with sampling lines facing outside of boat.

! Secure platform to gunnel cleat with a large plastic glove.

! Position Geo-Pump onto sampling platform and connect to battery with cables.

! Insert the canopy frame onto the sampling platform.

! Place a large clear plastic bag over the canopy frame, and secure bag with tape.

- Position tubs containing supplies and other sampling equipment in appropriate locations in the boat.

- The trolling motor battery and Geo-Pump battery should be located far astern, away from clean sampling apparatus in center, starboard of boat.

<u>Cleaning Supplies for Land/Boat Sampling included in Set-Up:</u>

! A 10 gallon carboy for dilute acid waste disposal,

- A 1-gallon container filled 2/3 full with 2% HNO_3 from the 4 liter carboy supplied by WSLH and used for tubing rinses and cleaning.

- Squirt bottles of both deionized water and 2% HNO_3 are included in set-up.

iii. Labeling In-Field

- Label according to master sampling plan prior to or immediately after sample is collected.

- Label with Sharpie, the outer bags and the sample bottle with the site code, date, and type of sample (unfiltered, filtered, duplicate, blank).

- Record the same information on the **Test Request Form**. (A number was already assigned by the Wisconsin's lab and marked on the bottle. This number was added to the Test Request Form for sample identification).

- A blank **Test Request Form** is shown in **Figure 2**.

iv. Tube Line Sampling

- Insert clean 18" Teflon tubing into pump head.

- Assemble Teflon sampling line (25 ft or 60 ft), Teflon line weight and Kevlar support rope.

FIGURE 2
Test Request Form

Wisconsin State Laboratory of Hygiene INORGANIC TEST REQUEST FORM
Form: INDIANA 4-98

Field No.: ____________ Site Name: ____________

Sample Location/Description: ____________

Send Report To: Dr. Syed M. GhiasUddin
Indiana Department Of Environmental Management
Office of Water Management
100 North Avenue
PO Box 6014
Indianapolis, IN 46206-6015

Account Number: IN001

Collected By: ____________

Phone: (___) ___-____

Sample Type:
__ Surface Water
__ Blank

Depth of Sample (feet or meters) __ ___ F or M

Unusual Occurrences:

Begin or Grab Date __/__/__ MM DD YY
Begin Time (24 hr clock) __:__
End Date - For Composite Samples Only __/__/__ MM DD YY
End Time (24 hr clock) - For Composite Samples Only __:__

Suspended Particulate Matter
__ SPM 0.4u (ctr) Filter# ____ Volume ____ ml
__ SPM 0.4u (ctr) Filter# ____ Volume ____ ml

500 ml Teflon
__ Dissolved Mercury Bottle #____
__ Total Mercury Bottle #____

250 ml Teflon
__ Dissolved Metals Bottle #____
__ Total Recoverable Metals Bottle #____

125 ml Teflon Bottle #____
__ Dissolved Hexavalent Chromium

500 ml Polyethylene Bottle #____
__ Dissolved Nitrate __ Dissolved Sulfate
__ Dissolved Chloride __ Dissolved Alkalinity
__ Total Dissolved Solids

250 ml Glass Bottle #____
__ Total Dissolved Phosphorus
__ Dissolved Kjeldahl Nitrogen
__ Dissolved Organic Carbon

250 ml Polyethylene Bottle #____
__ Total Solids or Total Dissolved Solids
(Please circle choice)

Additional Comments/Parameters

Chain of Custody

Date Shipped from Field: ____________

Signature: ____________

Date Received at WSLH: ____________

Signature: ____________

- Attach line weight to end of sampling line (make sure that tubing is completely inserted into fitting at top of weight and that nut is fastened tightly). Tie Kevlar rope to loop of Teflon string attached to sampling-line weight.

- If in a boat, insert weight through receptacle on end of boom and lower into river/lake to first depth and secure Kevlar support rope onto starboard plastic cleat

.

- Keep remainder of sampling line tubing in plastic bag until pump head tubing is attached.

v. Boom Installation on Boat (Gloves Required)

- Hook fiberglass cleat adaptor into place on bow cleat.

- Put boom in place by resting in fiberglass cleat adaptor, hooking straight end under bungie cord, and securing boom in fiberglass cleat by tying with an arm-length glove.

vi. Geo-Pump Loading and Sample Line Connection (Clean-Hands, Dirty-Hands)

- Load pump-head tubing into Geo-Pump using “clean-hand dirty-hand” protocol.

- Open pump head clamp lever, insert tubing into pumphead and then close clamp lever making sure that tubing is properly positioned.

- At this point, retrieve open end of sampling line from storage bag and insert it into pump head tubing.

- Clean-hands opens inner bags only and Dirty-hands opens outer bags only.

- “Dirty-hands” open outer bag of Teflon Clamp Ring (TCR) and “Clean-hands” open inner bag, remover TCR and slides it onto plexiglass sampling platform.

- Using the same “Clean-hands Dirty-hands” (Remember, clean bag always remains inside of dirty bag or outer bag) technique, remove Teflon Tubing Adaptor Fitting (TTAF).

- Then remove short Teflon tubing section (~12 ”) and insert and tighten the TTAF onto the Teflon tubing section.

- Insert the opposite end of tubing section into outlet side of pump head tubing and then secure the TTAF end of tubing section to plexiglass platform using TCR.

vii. Unfiltered Sample Collection

- Start Geo-pump and adjust to high speed to flush lines (no splashing). Flush lines for a minimum of 5 minutes before unfiltered samples are collected.

- Partially fill (1/8 full) Trace Metal sample bottle from water stream. Bottle is loosely capped and gently shaken to rinse. Repeat this process 3 times.

- Collect sample under water stream. Make sure to leave enough room to add preservatives.

- Place into original inner-bag and reseal. Do not reseal outer-bag until preservatives are added. Protect bottles by placing into cooler.

- Mercury sample bottles are supplied partially filled with dilute HCl. Dump acid into waste container (25 L Carboy).

- Partially fill (1/8 full) sample bottle under water stream. Loosely cap and gently shake to rinse. Pour into waste container and repeat for a total of 3 bottle rinses.

- On the fourth collection, fill the bottle. Be careful to leave enough room for preservatives.

- Return bottle to inner-bag and reseal. Do not seal outerbag until preservatives are added. Protect bottles by placing into cooler.

- SPM-Ancillary Sample Collection bottles are rinsed 3 times as described earlier.

- On the fourth collection, partially fill bottle, leaving room for preservatives where needed. Clean-hands should re-glove after handling the poly-bottle.

viii. Filtered Sample Collection

- After unfiltered samples have been collected, Dirty-hands turns off pump, retrieve a double-bagged Meissner filter and open outer bag. Clean-hands opens inner bag and removes filter capsule, opens vents, drains off storage MQ-water, and reseals vents.

- Remove TCL/TTAF assembly from sampling platform using 'clean hands dirty hands" techniques as always and screw the filter capsule onto TTAF.

- Then, re-insert TCL/TTAF/filter capsule assembly into sampling platform.

- Start Geo-pump and adjust to moderate speed to flush capsule with one-liter, of distilled water from a graduated cylinder.

- Collect samples as before.

ix. Two Depth Sampling (Composite Two Depths Samples into One Sample)

- Collect shallow unfiltered samples first, only filling the bottles half full.
- Attach filter to TTAF and collect shallow filtered samples again, filling the bottles half full.
- Next lower sample line to the deeper depths and, after the line is flushed for 5 minutes, the last half of the samples are added to the filtered sample bottles.
- The filter is then removed and the last half of the unfiltered sample from the lower depth is added to the original unfiltered sample bottles. Mix.

x. Cleaning

- Rinse sampling platform and table with dilute acid and then with clean water.
- Put platform back into storage containers for transport back to lab.
- Rinse platform with Deionized water in laboratory, reseal with clean bags, and put back into storage tub.
- Supplies, such as tubing, are sent back to Wisconsin's lab for cleaning.
- Dispose of used gloves, plastic bags, wipes, and glass into large bag marked WASTE.
- Clean tarp and boat by rinsing with water.

xi. Preservatives

- Clean off area to work on either on plastic table in-field or on flat tub in-boat.
- Cover work area with clean plastic bags.
- Remove preservatives using 'clean hands, dirty hands' from storage and set out on work area for easy access.
- Set out samples that need to be preserved and sort according to preservatives needed.
- Add preservatives to sample.
- Dispose of empty preservative containers into bag marked RECYCLED WASTE. (Send back to Wisconsin lab for cleaning and reuse).
- Tightly fasten lid of preserved sample bottles and shake.
- Replace sample bottle into plastic bag and put into cooler.
- A complete schematic for water sample collection, sample filtration, preservation, and

other steps including those to prepare the samples for both shipment and analysis are described in **Figure 3**.

c. Filtration of Water Samples for Suspended Particulates (SP) and Measurement of Nutrients and Alkalinity

- **Apparatus Set-Up and Filtration:** This procedure requires a Plastic Filtration apparatus, PCTE filters and a hand pump. These apparatus and other necessary tools and accessories were provided by the WSLH for this project. For the Suspended Particulates, unfiltered water sample collected in 500 polyethylene bottle from each sampling site or location was used and processed through this filtering apparatus on the same sampling day. Before filtration, a 0.4 um PCTE filter provided in preweighed petri dish was loaded on a platform into Filtration apparatus and carefully screwed on top. An aliquot of 25 ml of unfiltered water sample was poured and filtered first through the filter and discarded to rinse the filter and the apparatus with the water sample from a given site or location. Subsequently, 225 ml of unfiltered water sample (three aliquots of 75 ml each) was filtered through and each time the volume faltered was recorded on the "**Test Request Form**". Filtration of each water sample was assisted by applying a suction (< 20 psi) through the use of a Hand pump. The Filter containing the Particulates was saved for SP measurement, while the filtrate and the remaining unfiltered water sample were saved for Nutrient and Alkalinity measurements.

d. Quality Assurance/Quality Control (QA/QC) for Sampling and Analysis:

In 1998 a **Quality Assurance Project Plan** (**QAPP**) exclusive for the Trace Metal Pilot Project was prepared by IDEM and supplied to WSLH . This QAPP was enforced throughout this project and additional QA/QC procedures were followed, both in the field and in the analytical laboratory, to ensure that the metal data collected is of high quality.

The following is a list of QA/QC procedures that were implemented for this pilot project.

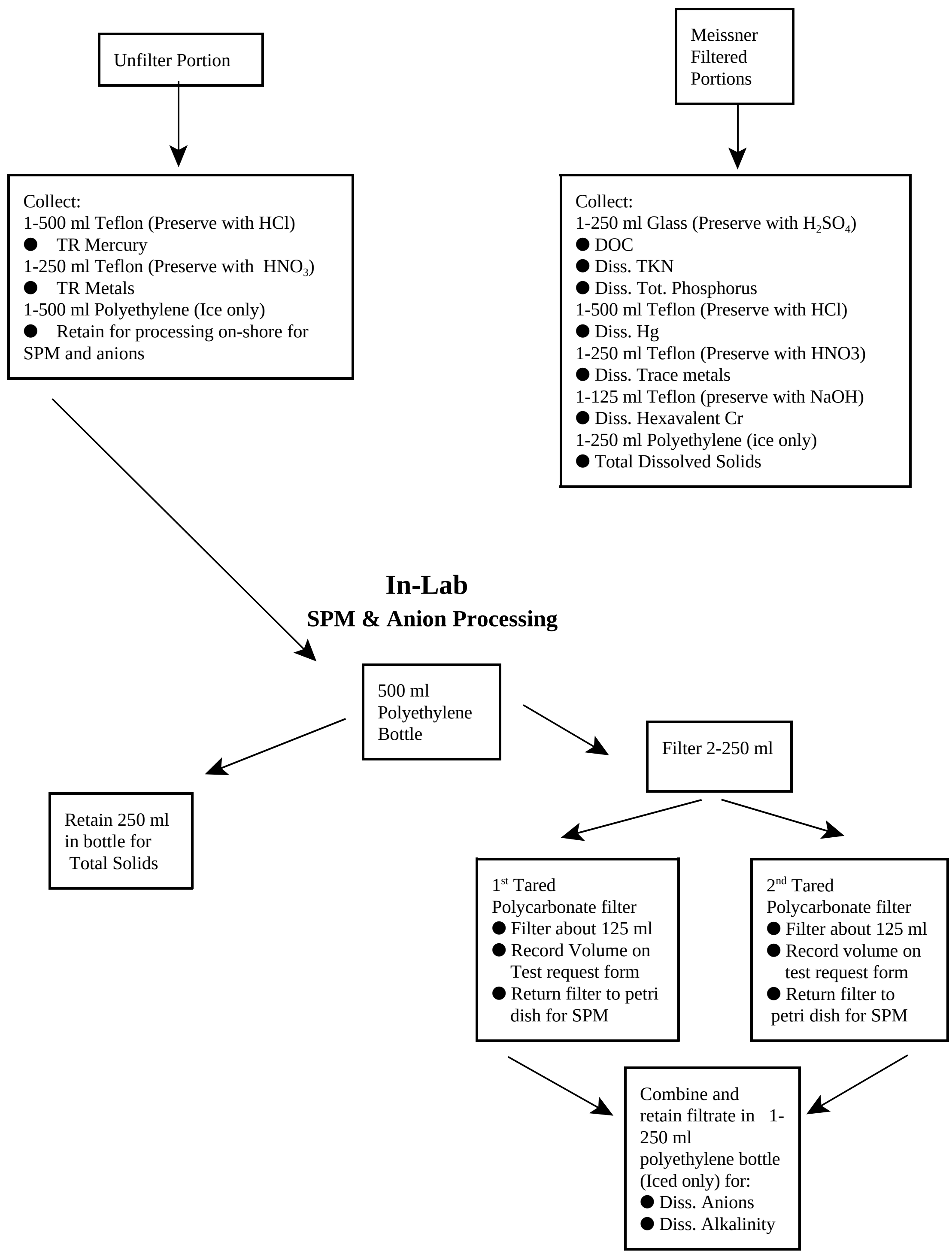
i. In-Field QA Blank Collection Procedures:

For Quality Control and/or **Field or Equipment blanks**, IDEM staff strictly followed a 9 step **Blanking Protocol** as described and provided by WSLH. This protocol for the most part was identical to the one also used for collection of water samples.

- Label three sets (250 ml trace metal, 500 ml mercury) of bottles as follows: **Source Water, Filter Blank,** and **Tubing Blank.** Record each Sample Bottle number and type on "Test Request Form".

FIGURE 3
Schematic For Sampling and Processing Surface Water

In-Field Processing



- Set up filtration platform in the field as usual. Install a new section of pump head tubing in Peristaltic Pump. Attach Teflon Tubing Adaptor Fitting (TTAF) and lock in Teflon Clamp Ring (TCR). Uncouple tubing weight from sample line.

- Remove Teflon cap from the 5 L Milli-Q (MQ) bottle, replace it with another cap with a hole and save the original Cap in a Zip-lock bag. Insert short length of Teflon tubing into MQ bottle and connect the other end of the tubing to the pump head tubing in Peristaltic Pump. Place a plastic bag over 5 L bottle to isolate it from the atmosphere during blanking procedure.

- Flush approximately 500 ml of blank water through pump head tubing. Collect **Source Water** sample as per the sampling protocol, with appropriate number of rinses. Conserve water as much as possible. Shut off Peristaltic Pump when not collecting samples or flushing.

- Remove Teflon tubing from 5 L bottle and place into 3 L bottle. Rinse with MQ water. Connect a filter cartridge to TTAF and lock into holder. Flush approximately 100 ml of Rinse MQ through Meisner filter cartridge. Place Teflon tubing back into 5 L blank water bottle and collect **Filter Blank** samples as per the sampling protocol.

- Remove Meisner filter cartridge (save for later use). Uncouple short Teflon line and save in a Zip-Lock bag. Insert one end of **Teflon sampling line** (**Teflon tubing, 40 - 60 feet**) into 3 L bottle and connect other end of Teflon tubing to peristaltic pump. Flush approx. 1000 ml of Rinse MQ through Teflon sampling line. Place sample tubing line into 5 L blank water bottle and collect **Tubing Blank** sample as per the sampling protocol.

- Preserve each blank (**Source Blank, Filter Blank** and **Tubing Blank**) as per the sampling protocol.

- Recap 3 L and 5 L MQ bottles with the respective caps that were saved in a Zip-lock bag. Place all blank samples bottles, 3 and 5 L bottles, short Teflon tubing in Blank Kit Cooler and return to WSLH for analysis.

- After the Blanking procedure is completed, attach **Tubing Weight** to Teflon sampling line (Fasten Securely) to begin sampling of ambient water.

- A complete schematic for blanking procedures for collection of Field or Equipment Blanks is further illustrated and described in **Figure 4**.

For the field QA, the following samples were collected:

- **Field or Equipment Blanks:** Field blanks were collected before water samples collection. Field blanks will demonstrate that contamination has not occurred during sampling and sample processing. The field blanks were generated by filling an appropriate large container with reagent water in the Laboratory by WSLH, transporting the filled container to the sampling site, processing reagent water through each of the surface water sample processing steps and equipment that were used in the field. At least one field blank was collected for every 10 samples or each sampling event. This sample is identified as **Source Blank**. **Field or Equipment Blanks** were run on all equipment that were used in the field. This included collecting **Bottle Blank or Source Blank, Filter Blank and Tubing Blank**.

- To estimate the level of metal contamination from the sample tubing line, filter cartridge, and general handling of the sampling apparatus. Blanking Procedures were completed before beginning normal sampling.

- **Field Duplicates:** The **Field Duplicates** were collected by collecting two water samples in rapid succession. At least one Field duplicate was collected for every 10 samples, and/or at each sampling event. (Except on one occasion, during the May first sampling event, no field duplicate was collected. The Contractor (WSLH) within the lab split one water sample and ran the split samples as a duplicate.)

- **Chain-of-Custody**: Chain-of-Custody is the sequence of persons who have the possession of an item or an environmental sample (e.g. water sample) in custody. Chain-of-Custody is demonstrated by documenting that the item in question was always in a state of custody. This is accomplished through a combination of field and laboratory records that demonstrate possession and transfer of custody.

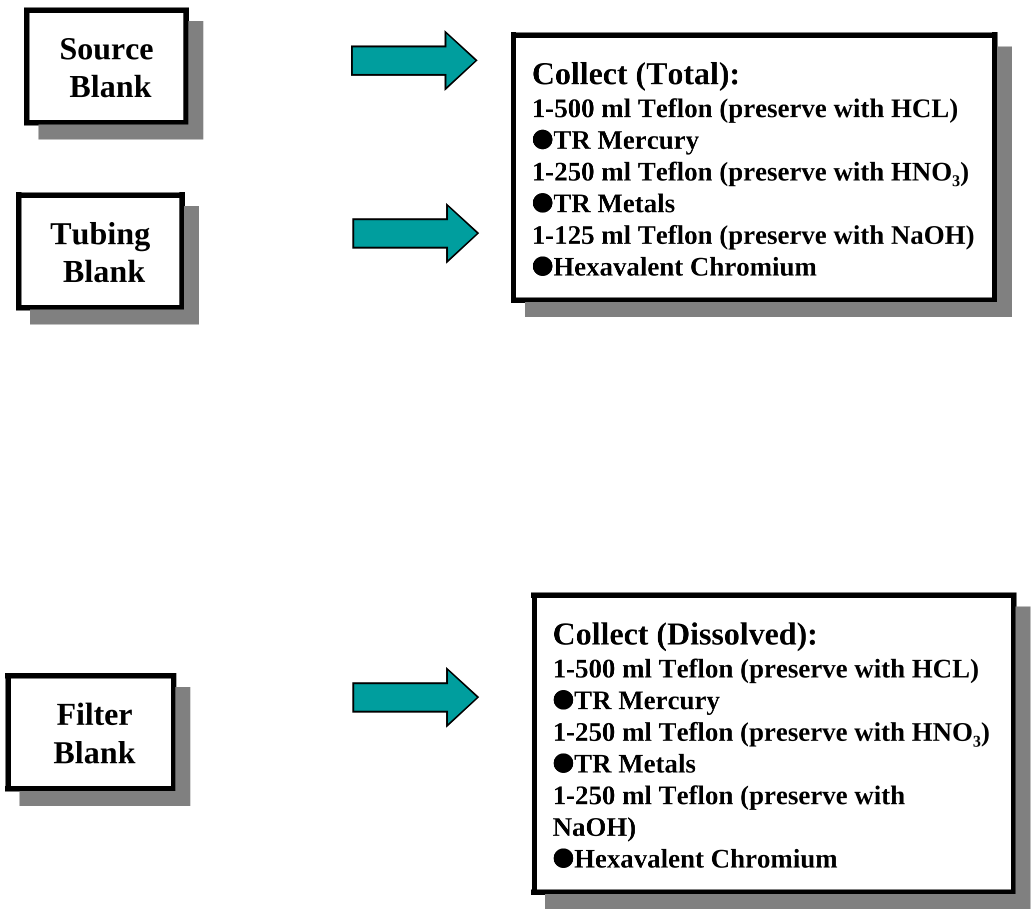
- A **Chain-of-Custody Statement** was included on the "**Test Request Form**" (see **Figure 2**). After the Test Request Form was completed and the sample bottles were properly labeled and numbered, the Chain-of Custody was signed, sealed in zip-lock bag and returned to WSLH in the shipping container along with the samples.

- **Labeling and Sample Identification**: Sample bottles were received from WSLH with the sample numbers and parameter already marked on the bottles. As each sample bottle was picked up and used for collecting the water sample, the sample bottle number was noted on the "**Test Request Form**" (**Figure 2**) for the indicated parameter for analysis. In addition, after the water sample was collected, as a cautionary measure and for proper identification of each sample bottle, the sampling date, and if the water sample is filtered or unfiltered, were written in permanent ink on the sample bottle.

- **Sample Storage & Shipment:** Immediately after water samples were collected, all the sample bottles were stored in an ice chest 1/3rd filled with cubed ice to achieve a temperature of 4°C. For sample preservation, sample bottles were removed from the storage container temporarily, and, after the preservatives were added, all the sample bottles were returned to the ice storage container. Ice was replenished in IDEM's lab before shipment by Federal Express for overnight delivery to WSLH, to insure that 4°C temperature was maintained throughout handling and shipping.

FIGURE 4

Schematic for Field or Equipment Blanks



ii. In-Lab QA/QC Procedures

The WSLH performed the following Quality Control procedures during the analysis to insure that the analytical runs were within control parameters. The in-lab QC tasks performed by WSLH were as follows:

- **Samples for Matrix Spike and Matrix Spike Duplicate:** Water samples were spiked with standard spike solutions in the lab before analysis for Matrix Spike (MS) and Matrix Spike Duplicate (MSD) for **Precision and Recovery**. At least, one MS/MSD was used for every 10 water samples analyzed.

- **Field Duplicate:** At each sampling event, a field duplicate sample was taken. However, in the May 1998 sampling event, a field duplicate was not taken and the laboratory split one sample and ran the split sample as a duplicate.

- **Method Blank:** A laboratory blank was prepared and processed with each analysis set to check if any contaminants were introduced during the analyses process.

- **Quality Control (QC):** For quality control, with each analytical run, WSLH performed the following additional analyses to insure that the sample analyses procedures were within control and all the analytical results are valid. The following is a list of Quality Control checks that the WSLH routinely conducted for this project.

QC Type	Description
QCS	Quality Control Sample
OPR	On-going Precision and recovery
CCV	Continuing Calibration Verification Check
ICB	Initial Calibration Blank
CCB	Continuing Calibration Blank
D	Laboratory Duplicate Analysis
MS	Laboratory Duplicate Analysis
MSD	Laboratory Matrix Spike Duplicate
ND	Not Detected, Result is below the Method Detection Limit

e. Safety:

- Personnel safety in the field was followed during the entire process of field sampling. Personnel involved in sample collection will wear appropriate clothing and personal protective equipment when operating boats or sampling in deep water or swift currents.

RESULTS

Dissolved and Total Recoverable Metals:

Analytical results for individual dissolved and total recoverable metals and for several non-metal parameters received from the WSLH Contract Lab, and the Hydrolab field data for several parameters collected by IDEM staff from four separate sampling events, are listed in **Table 3** through **Table 6**.

For each sampling event, the Fall Creek Flow data was taken from **Gaging Station 03357500** near Fortville, which is downstream from the bridge on State Highway 238. The flow data and the $Q_{7,10}$ for the Fall Creek are provided at the end of each table. The flow data from the gaging station show that, as compared to low flow conditions ($Q_{7,10}$,15 cfs), due to unexpected heavy rains, Fall Creek mean flow conditions were typically high and ranged between 43 and 298 cfs during sampling in May, July, August and September, 1998 (see **Tables 3-6**).

The mean values for each of the dissolved and total recoverable metals and for several other parameters obtained from each site or location, sampled at four different times, and the minimum and maximum value for each and every parameter from each sampling location are listed in **Table 7 (**see **Pages 38 to 40)**.

A total of **20 Metals**, **11 Non-metals** and **5 Hydrolab** parameters were analyzed in ambient water samples collected from Fall Creek Watershed for the Trace Metal Project. With the exception of calcium, potassium, magnesium, and sodium, all metals were analyzed for dissolved and total recoverable metal concentrations. Calcium, potassium, magnesium and sodium were measured as dissolved metals only.

Except for the silver metal (**MDL 0.009 ug/L or LOQ 0.03 ug/L**), all the other 19 metals were detected in the ambient waters. Silver was not detected as dissolved or total metal at any of the site in Fall Creek. Other less frequently found metals in the surface water from Fall Creek were Beryllium and Iron in dissolved form (**Beryllium LOQ 0.04 ug/L, Iron LOQ 0.008 ug/L**). Occasionally dissolved Hexavalent Chromium, Lead and Mercury **(Cr-VI LOQ 1.5 ug/L, Lead LOQ 0.02 ug/L** and **Mercury LOQ 0.0003 ug/L**), were not found at one or more sampling sites (see **Tables 3 to 6**). All the remaining metals had frequent hits and were detected as both dissolved and total recoverable metals.

Among the several metals analyzed, ten metals (**Aluminum**, **Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Selenium, and Zinc**) were by far the most conspicuous metals detected and were detected as both dissolved and total recoverable metals at all the five sampling locations (see **Table 7**). The data also show that four metals (**Aluminum, Lead, Mercury, and Zinc**) were mostly present as total recoverable metals (**Aluminum 860 ug/L, Lead 2.3 ug/L, Mercury 4.5 ng/L, and Zinc 8 ug/L**) and the same metals were present in very small amounts as dissolved metals (**Aluminum 1.2 - 4.4 ug/L**, **Lead 0.016-0.312 ug/L**, **Mercury 0.0001 - 0.0018 ug/L (0.1-1.8 ng/L)**; and **Zinc 0.2 - 0.9 ug/L**). The respective

TABLE 3
Analytical Results From Sampling Event # 1
(May 4 and 5 1998)

PARAMETER	CAS Number	Test Method	MDL ug/L	LOQ ug/L	Sampling Locations				
					Site 1	Site 2	Site 3	Site 4	Site 5
METALS									
Aluminum, dissolved	7429-90-5	EPA1638	0.1	0.3	3.7	2.8	2.1	2.7	1.2
Aluminum, total recoverable	7429-90-5	EPA1638	0.1	0.3	326	479	180	82.3	68.5
Antimony, dissolved	7440-35-0	EPA1638	0.01	0.03	0.12	0.12	0.13	0.15	0.15
Antimony, total recoverable	7440-36-0	EPA1638	0.01	0.03	0.13	0.12	0.14	0.15	0.15
Arsenic, dissolved	7440-38-2	EPA1638	0.1	0.4	1.1	1.1	0.9	1	1
Arsenic, total recoverable	7440-38-2	EPA1638	0.1	0.4	1.9	2.1	1.6	1.6	1.6
Beryllium, dissolved	7440-41-7	EPA1838	0.01	0.04	ND	ND	ND	ND	ND
Beryllium, total recoverable	7440-41-7	EPA1638	0.01	0.04	0.02	0.03	0.01	ND	ND
Calcium, dissolved	7440-70-2	EPA3120B	6	20	81	78	65	57	57
Cadmium, dissolved	7440-43-9	EPA1638	0.01	0.03	ND	ND	ND	ND	ND
Cadmium, total recoverable	7440-43-9	EPA1638	0.01	0.03	0.03	0.05	0.01	ND	ND
Chromium, dissolved	7440-47-3	EPA1638	0.5	1.5	0.26	0.23	0.17	0.17	0.15
Chromium, total recoverable	7440-47-3	EPA1638	0.5	1.5	0.75	1.17	0.53	0.26	0.18
Chromium - III*	16065831	EPA1638	0.5	1.5	0.5	0.9	0.3	<0.2	<0.2
Chromium - VI, dissolved	18540299	EPA1636	0.5	1.5	0.2	0.3	0.2	0.2	0.3
Copper, dissolved	7440-50-8	EPA1638	0.01	0.04	0.75	0.7	0.84	0.84	0.84
Copper, total recoverable	7440-50-8	EPA1638	0.01	0.04	2.07	2.56	1.54	1.46	1.47
Iron dissolved	7439-89-6	EPA3120B	0.003 mg/l	0.008 mg/l	ND	ND	0.01	ND	ND
Iron, total recoverable	7439-89-6	EPA3120B	0.003 mg/l	0.008 mg/l	0.61	0.83	0.25	0.09	0.11
Lead, dissolved	7439-92-1	EPA1638	0.005	0.02	0.027	0.031	0.02	0.018	0.014
Lead, total recoverable	7439-92-1	EPA1638	0.005	0.02	0.785	1.45	0.403	0.186	0.185
Magnesium, dissolved	7439-95-4	EPA3120B	10	40	27	27	23	20	21
Manganese, dissolved	7439-96-5	EPA1638	0.01	0.03	21.5	29.7	0.54	0.63	2.77
Manganese, total recoverable	7439-96-5	EPA1638	0.01	0.03	49.9	59	18	18	19
Mercury, dissolved	7439-97-6	EPA1631	0.0001	0.0003	0.31	0.55	0.57	0.52	0.59
Mercury, total recoverable	7439-97-6	EPA1631	0.0001	0.0003	20.8	2.30	1.27	1.09	1.01
Nickel, dissolved	7440-02-0	EPA1638	0.09	0.3	1.64	1.41	1.27	1.23	1.18

PARAMETER	CAS Number	Test Method	MDL ug/L	LOQ ug/L	Sampling Locations				
					Site 1	Site 2	Site 3	Site 4	Site 5
Nickel, total recoverable	7440-02-0	EPA1638	0.09	0.3	2.64	3.12	2.23	2.06	1.66
Potassium, dissolved	7440-09-7	SM3111B	10	30	1.6	1.5	1.7	2	2
Selenium, dissolved	7782-49-2	EPA1638	0.3	1	1.3	1.3	1.4	1.2	1
Selenium, total recoverable	7782-49-2	EPA1638	0.3	1	1.5	1.3	1.4	1.5	1.2
Silver, dissolved	7440-22-4	EPA1638	0.009	0.03	ND	ND	ND	ND	ND
Silver, total recoverable	7440-22-4	EPA1638	0.009	0.03	ND	ND	ND	ND	ND
Sodium dissolved	7440-23-5	SM3120B	10	30	14	15	13	12	12
Thallium, dissolved	7440-28-0	EPA1638	0.004	0.012	0.035	0.029	0.03	0.028	0.031
Thallium, total recoverable	7440-28-0	EPA1638	0.004	0.012	0.057	0.066	0.052	0.046	0.051
Zinc, dissolved	7440-66-6	EPA1638	0.04	0.15	0.58	0.67	0.4	0.23	0.22
Zinc, total recoverable	7440-66-6	EPA1638	0.04	0.15	3.7	5.85	1.77	1.01	0.89
NON-METAL PARAMETERS									
Alkalinity, dissolved	E-14506	EPA310.1	1 mg/l	3 mg/l	245	244	204	179	178
Chloride, dissolved	16887006	EPA300.0	0.02 mg/l	0.08 mg/l	30.2	32.6	28.4	26.7	25.4
Hardness (as $CaCO_3$)	E-11778	SM2340	0.1 mg/l	0.4 mg/l					
Nitrogen, nitrate, dissolved	14797558	EPA300.0	0.003 mg/l	0.01 mg/l	3.68	3.5	2.97	2.35	2.29
Nitrogen, total (TKN), dissolved	E-10264	JWPCF	0.2 mg/l	1 mg/l	0.3	0.2	0.4	0.5	ND
Organic carbon, dissolved (DOC)	N/A	SM5310B	0.3 mg/l	1 mg/l					
Phosphorus, dissolved	7723140	SM4500PF	0.002 mg/ll	0.006 mg/l	0.031	0.03	0.012	0.012	0.009
Solids, filterable residue (TDS)	E-10173	SM2540C	7 mg/l	28.6 mg/l	406	410	348	316	320
Solids, total residue (TS)	E-10151	SM2540B	7 mg/l	28.6 mg/l	458	462	362	340	340
Sulfate, dissolved	14808798	EPA300.0	0.01 mg/l	0.05 mg/l	43	42.7	36	34.3	33.1
Suspended particulate matter (SPM)	N/A	S&P IV	0.08 mg/l	0.27 mg/l	21.8	24.5	10.4	8.93	8.84
HYDROLAB PARAMETERS									
Dissolved oxygen (DO)	E-14539	SM4500-O	0.01 mg/l	0.03 mg/l	10.6	8.6	14.0	8.9-15.4	9.6
pH	N/A	SM4500H	0.01 SU	0.03 SU	8.4	8.23	8.85	8.6-9.0	8.9
Specific conductance	N/A	SM2510	1 umhos/cm	3 umhos/cm	634	632	522	469-491	484

Turbidity	N/A	SM2130	0.1 NTU	0.3 NTU					
PARAMETER	CAS Number	Test Method	MDL ug/L	LOQ ug/L	Sampling Locations				
					Site 1	Site 2	Site 3	Site 4	Site 5
Water temperature	N/A	SM2550	0 ºC	-5 ºC	14.9	15.2	15.6	14.8-18.3	17.4

Fall Creek Flow Data from Gaging Station 03351500 Near Fortville, IN, Downstream from Bridge on State Highway 238.	Sampling Date	Flow (cfs)	Mean Flow (cfs)
* Usual $Q_{7, 10}$ = 15 cfs	5/4/1998 5/5/1998	285 235	260

TABLE 4
Analytical Results From Sampling Event # 2.
(July 15, 16, 21, and 23 1998)

PARAMETER	CAS Number	Test Method	MDL ug/L	LOQ ug/L	Sampling Locations				
					Site 1	Site 2	Site 3	Site 4	Site 5
METALS									
Aluminum, dissolved	7429-90-5	EPA1638	0.1	0.3	3.1	39.4	3.65	3.64	2.5
Aluminum, total recoverable	7429-90-5	EPA1638	0.1	0.3	200	780	670	140	95
Antimony, dissolved	7440-35-0	EPA1638	0.01	0.03	ND	0.17	0.18	0.17	0.18
Antimony, total recoverable	7440-36-0	EPA1638	0.01	0.03	0.14	0.16	0.19	0.17	0.18
Arsenic, dissolved	7440-38-2	EPA1638	0.1	0.4	1.6	1.7	1.8	2	1.8
Arsenic, total recoverable	7440-38-2	EPA1638	0.1	0.4	1.7	1.9	2.2	2.2	1.9
Beryllium, dissolved	7440-41-7	EPA1838	0.01	0.04	0.14	ND	ND	ND	ND
Beryllium, total recoverable	7440-41-7	EPA1638	0.01	0.04	ND	0.02	0.01	ND	ND
Calcium, dissolved	7440-70-2	EPA3120B	6	20	82	50	56	52	53
Cadmium, dissolved	7440-43-9	EPA1638	0.01	0.03	0.01	ND	ND	ND	ND
Cadmium, total recoverable	7440-43-9	EPA1638	0.01	0.03	0.02	0.04	0.02	ND	ND
Chromium, dissolved	7440-47-3	EPA1638	0.5	1.5	0.19	0.25	0.16	0.18	0.18
Chromium, total recoverable	7440-47-3	EPA1638	0.5	1.5	2.09	2.06	1.68	1.12	0.502
Chromium - III*	16065831	EPA1638	0.5	1.5	2.09	1.942	1.548	1.069	0.491
Chromium - VI, dissolved	18540299	EPA1636	0.5	1.5	ND	ND	ND	ND	ND
Copper, dissolved	7440-50-8	EPA1638	0.01	0.04	0.98	1.77	0.96	1.05	1.02
Copper, total recoverable	7440-50-8	EPA1638	0.01	0.04	1.37	3.18	2.18	1.33	1.52
Iron dissolved	7439-89-6	EPA3120B	0.003 mg/l	0.008 mg/l	ND	0.05	ND	ND	ND
Iron, total recoverable	7439-89-6	EPA3120B	0.003 mg/l	0.008 mg/l	0.33	1	0.76	0.17	0.16
Lead, dissolved	7439-92-1	EPA1638	0.005	0.02	0.016	0.081	0.016	0.007	0.011
Lead, total recoverable	7439-92-1	EPA1638	0.005	0.02	0.411	1.38	1.17	0.224	0.194
Magnesium, dissolved	7439-95-4	EPA3120B	10	40	30	17	25	19	18
Manganese, dissolved	7439-96-5	EPA1638	0.01	0.03	21	14	1.11	8.67	3.66
Manganese, total recoverable	7439-96-5	EPA1638	0.01	0.03	33	47	62	56	19
Mercury, dissolved	7439-97-6	EPA1631	0.0001	0.0003	0.4	1.84	0.44	0.5	1.04
Mercury, total recoverable	7439-97-6	EPA1631	0.0001	0.0003	1.24	4.26	2.94	1.34	1.08
Nickel, dissolved	7440-02-0	EPA1638	0.09	0.3	2.00	1.83	1.53	1.45	1.52

PARAMETER	CAS Number	Test Method	MDL ug/L	LOQ ug/L	Sampling Locations				
					Site 1	Site 2	Site 3	Site 4	Site 5
Nickel, total recoverable	7440-02-0	EPA1638	0.09	0.3	3.75	3.61	3.09	1.98	2.04
Potassium, dissolved	7440-09-7	SM3111B	10	30	19	9.9	15	9.9	9.3
Selenium, dissolved	7782-49-2	EPA1638	0.3	1	1.2	0.8	0.9	1.0	0.4
Selenium, total recoverable	7782-49-2	EPA1638	0.3	1	2.1	0.9	1	1	1.2
Silver, dissolved	7440-22-4	EPA1638	0.009	0.03	ND	ND	ND	ND	ND
Silver, total recoverable	7440-22-4	EPA1638	0.009	0.03	ND	ND	ND	ND	ND
Sodium dissolved	7440-23-5	SM3120B	10	30	2.36	3.31	2.3	2.82	2.81
Thallium, dissolved	7440-28-0	EPA1638	0.004	0.012	0.021	0.015	0.006	ND	0.009
Thallium, total recoverable	7440-28-0	EPA1638	0.004	0.012	0.023	0.035	0.022	0.076	0.019
Zinc, dissolved	7440-66-6	EPA1638	0.04	0.15	0.89	0.81	0.5	0.49	0.33
Zinc, total recoverable	7440-66-6	EPA1638	0.04	0.15	2.08	5.16	4.18	0.93	0.81
NON-METAL PARAMETERS									
Alkalinity, dissolved	E-14506	EPA310.1	1 mg/l	3 mg/l	274	162	201	181	180
Chloride, dissolved	16887006	EPA300.0	0.02 mg/l	0.08 mg/l	41.1	21.9	32	21.8	21.2
Hardness (as $CaCO_3$)	E-11778	SM2340	0.1 mg/l	0.4 mg/l	330	200	240	210	210
Nitrogen, nitrate, dissolved	14797558	EPA300.0	0.003 mg/l	0.01 mg/l	2.4	2.98	0.87	1.15	1.7
Nitrogen, total (TKN), dissolved	E-10264	JWPCF	0.2 mg/l	1 mg/l	0.26	0.64	0.28	0.66	0.57
Organic carbon, dissolved (DOC)	N/A	SM5310B	0.3 mg/l	1 mg/l	2.2	5.1	3	3.7	4
Phosphorus, dissolved	7723140	SM4500PF	0.002 mg/ll	0.006 mg/l	0.039	0.083	0.011	0.011	0.013
Solids, filterable residue (TDS)	E-10173	SM2540C	7 mg/l	28.6 mg/l	456	290	320	272	286
Solids, total residue (TS)	E-10151	SM2540B	7 mg/l	28.6 mg/l	506	370	416	322	340
Sulfate, dissolved	14808798	EPA300.0	0.01 mg/l	0.05 mg/l	60.6	35	46	31	29.8
Suspended particulate matter (SPM)	N/A	S&P IV	0.08 mg/l	0.27 mg/l	5.81	16.4	18.4	6.86	1.43
HYDROLAB PARAMETERS									
Dissolved oxygen (DO)	E-14539	SM4500-O	0.01 mg/l	0.03 mg/l	9.0	7.3	6.05	4.0-8.3	7.40
pH	N/A	SM4500H	0.01 SU	0.03 SU	8.4	8.16	8.7	8.1-8.5	8.33
Specific conductance	N/A	SM2510	1 umhos/cm	3 umhos/cm	740	468	562	476-485	490

PARAMETER	CAS Number	Test Method	MDL ug/L	LOQ ug/L	Sampling Locations				
					Site 1	Site 2	Site 3	Site 4	Site 5
Turbidity	N/A	SM2130	0.1 NTU	0.3 NTU	10.8	46.2	49.1	9.5-12	5.75
Water temperature	N/A	SM2550	0 ºC	-5 ºC	24	26.7	27.6	27-28	27

Fall Creek Flow Data from Gaging Station 03351500 Near Fortville, IN, Downstream from Bridge on State Highway 238.	Sampling Date	Flow (cfs)	Mean Flow (cfs)
* Usual $Q_{7, 10}$ = 15 cfs	7/15/1998 7/16/1998 7/21/1998 7/23/1998	106 103 241 743	298

TABLE 5
Analytical Results From Sampling Event # 3
(August 10, 11, and 12 1998)

PARAMETER	CAS Number	Test Method	MDL ug/L	LOQ ug/L	Sampling Locations				
					Site 1	Site 2	Site 3	Site 4	Site 5
METALS									
Aluminum, dissolved	7429-90-5	EPA1638	0.1	0.3	4.4	3.1	4.4	5	4.1
Aluminum, total recoverable	7429-90-5	EPA1638	0.1	0.3	260	640	320	110	160
Antimony, dissolved	7440-35-0	EPA1638	0.01	0.03	0.13	0.14	0.17	0.18	0.18
Antimony, total recoverable	7440-36-0	EPA1638	0.01	0.03	0.14	0.16	0.19	0.19	0.18
Arsenic, dissolved	7440-38-2	EPA1638	0.1	0.4	1.6	1.9	2	2	1.8
Arsenic, total recoverable	7440-38-2	EPA1638	0.1	0.4	1.6	2.1	2.4	2	1.9
Beryllium, dissolved	7440-41-7	EPA1838	0.01	0.04	ND	ND	ND	ND	ND
Beryllium, total recoverable	7440-41-7	EPA1638	0.01	0.04	ND	0.02	ND	ND	ND
Calcium, dissolved	7440-70-2	EPA3120B	6	20	80	78	51	46	49
Cadmium, dissolved	7440-43-9	EPA1638	0.01	0.03	0.02	0.02	0.01	ND	ND
Cadmium, total recoverable	7440-43-9	EPA1638	0.01	0.03	0.03	0.04	0.02	ND	0.01
Chromium, dissolved	7440-47-3	EPA1638	0.5	1.5	0.06	0.04	0.04	0.03	0.03
Chromium, total recoverable	7440-47-3	EPA1638	0.5	1.5	0.49	1.06	0.46	0.14	0.21
Chromium - III*	16065831	EPA1638	0.5	1.5	0.4	1	0.4	<0.2	<0.2
Chromium - VI, dissolved	18540299	EPA1636	0.5	1.5	ND	ND	ND	ND	ND
Copper, dissolved	7440-50-8	EPA1638	0.01	0.04	0.71	0.73	0.64	0.69	0.69
Copper, total recoverable	7440-50-8	EPA1638	0.01	0.04	1.58	1.87	1.31	0.88	0.93
Iron dissolved	7439-89-6	EPA3120B	0.003 mg/l	0.008 mg/l	ND	ND	ND	ND	0.01
Iron, total recoverable	7439-89-6	EPA3120B	0.003 mg/l	0.008 mg/l	0.45	0.92	0.4	0.11	0.23
Lead, dissolved	7439-92-1	EPA1638	0.005	0.02	0.026	0.091	0.026	ND	0.007
Lead, total recoverable	7439-92-1	EPA1638	0.005	0.02	0.57	1.36	0.766	0.145	0.259
Magnesium, dissolved	7439-95-4	EPA3120B	10	40	29	28	25	20	20
Manganese, dissolved	7439-96-5	EPA1638	0.01	0.03	18.3	27.3	0.7	0.45	5.03
Manganese, total recoverable	7439-96-5	EPA1638	0.01	0.03	41	86	56	19	32
Mercury, dissolved	7439-97-6	EPA1631	0.0001	0.0003	0.29	0.1	0.17	ND	0.14
Mercury, total recoverable	7439-97-6	EPA1631	0.0001	0.0003	1.65	2.01	1.32	0.51	0.84
Nickel, dissolved	7440-02-0	EPA1638	0.09	0.3	2.36	2.54	1.72	1.68	1.4

PARAMETER	CAS Number	Test Method	MDL ug/L	LOQ ug/L	Sampling Locations				
					Site 1	Site 2	Site 3	Site 4	Site 5
Nickel, total recoverable	7440-02-0	EPA1638	0.09	0.3	3.38	4.05	2.67	2.02	2.33
Potassium, dissolved	7440-09-7	SM3111B	10	30	18	18	16	11	11
Selenium, dissolved	7782-49-2	EPA1638	0.3	1	0.6	0.5	0.4	0.7	0.6
Selenium, total recoverable	7782-49-2	EPA1638	0.3	1	0.9	0.7	1.2	0.7	0.8
Silver, dissolved	7440-22-4	EPA1638	0.009	0.03	ND	ND	ND	ND	ND
Silver, total recoverable	7440-22-4	EPA1638	0.009	0.03	ND	ND	ND	ND	ND
Sodium dissolved	7440-23-5	SM3120B	10	30	2.1	2.1	2.1	2.3	2.5
Thallium, dissolved	7440-28-0	EPA1638	0.004	0.012	0.015	0.009	0.006	ND	0.004
Thallium, total recoverable	7440-28-0	EPA1638	0.004	0.012	0.023	0.034	0.021	0.012	0.006
Zinc, dissolved	7440-66-6	EPA1638	0.04	0.15	0.83	0.46	0.35	0.21	0.27
Zinc, total recoverable	7440-66-6	EPA1638	0.04	0.15	3.02	5.42	2.56	0.59	1
NON-METAL PARAMETERS									
Alkalinity, dissolved	E-14506	EPA310.1	1 mg/l	3 mg/l		265	188	166	177
Chloride, dissolved	16887006	EPA300.0	0.02 mg/l	0.08 mg/l	37.5	37.6	33.1	24.5	24.4
Hardness (as $CaCO_3$)	E-11778	SM2340	0.1 mg/l	0.4 mg/l	320	310	230	200	210
Nitrogen, nitrate, dissolved	14797558	EPA300.0	0.003 mg/l	0.01 mg/l	ND	1.42	0.121	0.307	0.535
Nitrogen, total (TKN), dissolved	E-10264	JWPCF	0.2 mg/l	1 mg/l	0.4	0.31	0.64	0.48	0.42
Organic carbon, dissolved (DOC)	N/A	SM5310B	0.3 mg/l	1 mg/l	2.7	2.7	3.1	3.7	3.5
Phosphorus, dissolved	7723140	SM4500PF	0.002 mg/ll	0.006 mg/l	0.075	0.053	0.012	0.011	0.01
Solids, filterable residue (TDS)	E-10173	SM2540C	7 mg/l	28.6 mg/l	422	408	308	260	272
Solids, total residue (TS)	E-10151	SM2540B	7 mg/l	28.6 mg/l	524	510	388	320	340
Sulfate, dissolved	14808798	EPA300.0	0.01 mg/l	0.05 mg/l	58	54	46	35	34
Suspended particulate matter (SPM)	N/A	S&P IV	0.08 mg/l	0.27 mg/l	8.32	20	19	7.42	10.9
HYDROLAB PARAMETERS									
Dissolved oxygen (DO)	E-14539	SM4500-O	0.01 mg/l	0.03 mg/l	7.9	9.6	13.4	8.5-9.8	7.95
pH	N/A	SM4500H	0.01 SU	0.03 SU	8.33	8.4	8.7	8.5-8.7	8.42
Specific conductance	N/A	SM2510	1 umhos/cm	3 umhos/cm	710	702	537	460-464	480

PARAMETER	CAS Number	Test Method	MDL ug/L	LOQ ug/L	Sampling Locations				
					Site 1	Site 2	Site 3	Site 4	Site 5
Turbidity	N/A	SM2130	0.1 NTU	0.3 NTU	1.4	38.9	40.2	13.8-18.8	11.4
Water temperature	N/A	SM2550	0 ºC	-5 ºC	22.95	24.8	27.8	26.8-26.9	26.3

Fall Creek Flow Data from Gaging Station 03351500 Near Fortville, IN, Downstream from Bridge on State Highway 238.	Sampling Date	Flow (cfs)	Mean Flow (cfs)
* Usual $Q_{7, 10}$ = 15 cfs	8/8/1998 8/9/1998 8/10/1998	100 120 94	105

TABLE 6
Analytical Results From Sampling Event # 4
(September 8, 9, and 10 1998)

PARAMETER	CAS Number	Test Method	MDL ug/L	LOQ ug/L	Sampling Locations				
					Site 1	Site 2	Site 3	Site 4	Site 5
METALS									
Aluminum, dissolved	7429-90-5	EPA1638	0.1	0.3	2.6	2.8	3.7	2.5	3.3
Aluminum, total recoverable	7429-90-5	EPA1638	0.1	0.3	65	860	540	220	230
Antimony, dissolved	7440-35-0	EPA1638	0.01	0.03	0.14	0.16	0.22	0.22	0.18
Antimony, total recoverable	7440-36-0	EPA1638	0.01	0.03	0.16	0.19	0.25	0.24	0.22
Arsenic, dissolved	7440-38-2	EPA1638	0.1	0.4	1.2	1.9	2.4	3.1	3.1
Arsenic, total recoverable	7440-38-2	EPA1638	0.1	0.4	1.4	2.1	2.5	3.1	3.2
Beryllium, dissolved	7440-41-7	EPA1838	0.01	0.04	ND	ND	ND	ND	ND
Beryllium, total recoverable	7440-41-7	EPA1638	0.01	0.04	ND	0.03	ND	ND	ND
Calcium, dissolved	7440-70-2	EPA3120B	6	20	80	77	49	42	42
Cadmium, dissolved	7440-43-9	EPA1638	0.01	0.03	0.03	0.02	0.02	0.01	0.01
Cadmium, total recoverable	7440-43-9	EPA1638	0.01	0.03	0.03	0.06	0.03	0.02	0.02
Chromium, dissolved	7440-47-3	EPA1638	0.5	1.5	0.18	0.07	0.06	0.1	0.15
Chromium, total recoverable	7440-47-3	EPA1638	0.5	1.5	0.34	1.63	0.64	0.31	0.39
Chromium - III*	16065831	EPA1638	0.5	1.5	<0.2	<0.2	<0.2	<0.2	<0.2
Chromium - VI, dissolved	18540299	EPA1636	0.5	1.5	1.1	1.1	0.3	1.1	1.2
Copper, dissolved	7440-50-8	EPA1638	0.01	0.04	0.61	0.56	0.29	0.23	0.28
Copper, total recoverable	7440-50-8	EPA1638	0.01	0.04	0.87	2.25	1.06	0.85	0.84
Iron dissolved	7439-89-6	EPA3120B	0.003 mg/l	0.008 mg/l	ND	ND	ND	ND	ND
Iron, total recoverable	7439-89-6	EPA3120B	0.003 mg/l	0.008 mg/l	0.12	1.2	0.54	0.23	0.36
Lead, dissolved	7439-92-1	EPA1638	0.005	0.02	0.53	0.016	ND	0.312	0.035
Lead, total recoverable	7439-92-1	EPA1638	0.005	0.02	0.807	2.25	1.31	0.832	0.473
Magnesium, dissolved	7439-95-4	EPA3120B	10	40	31	30	27	22	22
Manganese, dissolved	7439-96-5	EPA1638	0.01	0.03	16	58	0.41	0.4	4.09
Manganese, total recoverable	7439-96-5	EPA1638	0.01	0.03	21	110	72	49	57
Mercury, dissolved	7439-97-6	EPA1631	0.0001	0.0003	0.34	0.53	0.23	0.28	0.65
Mercury, total recoverable	7439-97-6	EPA1631	0.0001	0.0003	0.66	4.45	2.08	1.71	2.25
Nickel, dissolved	7440-02-0	EPA1638	0.09	0.3	2.5	2.32	1.73	1.26	1.33

PARAMETER	CAS Number	Test Method	MDL ug/L	LOQ ug/L	Sampling Locations				
					Site 1	Site 2	Site 3	Site 4	Site 5
Nickel, total recoverable	7440-02-0	EPA1638	0.09	0.3	2.71	4.32	3.17	1.9	2.02
Potassium, dissolved	7440-09-7	SM3111B	10	30	27	29	20	14	13
Selenium, dissolved	7782-49-2	EPA1638	0.3	1	0.8	0.6	0.6	0.5	0.6
Selenium, total recoverable	7782-49-2	EPA1638	0.3	1	0.7	0.6	0.7	0.6	0.7
Silver, dissolved	7440-22-4	EPA1638	0.009	0.03	ND	ND	ND	ND	ND
Silver, total recoverable	7440-22-4	EPA1638	0.009	0.03	ND	ND	ND	ND	ND
Sodium dissolved	7440-23-5	SM3120B	10	30	2.4	2.6	2.3	2.5	2.5
Thallium, dissolved	7440-28-0	EPA1638	0.004	0.012	0.02	0.011	ND	ND	0.004
Thallium, total recoverable	7440-28-0	EPA1638	0.004	0.012	0.024	0.031	0.015	0.008	0.011
Zinc, dissolved	7440-66-6	EPA1638	0.04	0.15	0.93	0.77	0.26	0.26	0.18
Zinc, total recoverable	7440-66-6	EPA1638	0.04	0.15	1.6	7.98	2.9	1.13	1.63
NON-METAL PARAMETERS									
Alkalinity, dissolved	E-14506	EPA310.1	1 mg/l	3 mg/l	267	260	189	163	165
Chloride, dissolved	16887006	EPA300.0	0.02 mg/l	0.08 mg/l	51.2	56.2	41.4	29.2	29
Hardness (as $CaCO_3$)	E-11778	SM2340	0.1 mg/l	0.4 mg/l	330	320	230	200	200
Nitrogen, nitrate, dissolved	14797558	EPA300.0	0.003 mg/l	0.01 mg/l	2.24	1.91	ND	ND	0.08
Nitrogen, total (TKN), dissolved	E-10264	JWPCF	0.2 mg/l	1 mg/l	0.2	0.55	0.33	0.34	0.42
Organic carbon, dissolved (DOC)	N/A	SM5310B	0.3 mg/l	1 mg/l	2.2	2.5	3.2	3.6	3.6
Phosphorus, dissolved	7723140	SM4500PF	0.002 mg/l	0.006 mg/l	0.05	0.53	0.009	0.009	0.012
Solids, filterable residue (TDS)	E-10173	SM2540C	7 mg/l	28.6 mg/l	456	458	328	268	262
Solids, total residue (TS)	E-10151	SM2540B	7 mg/l	28.6 mg/l	476	516	380	302	308
Sulfate, dissolved	14808798	EPA300.0	0.01 mg/l	0.05 mg/l	66	61	46	35	34
Suspended particulate matter (SPM)	N/A	S&P IV	0.08 mg/l	0.27 mg/l	1.07	31.8	22.4	1.98	12.1
HYDROLAB PARAMETERS									
Dissolved oxygen (DO)	E-14539	SM4500-O	0.01 mg/l	0.03 mg/l	8.3	13.9	12.3	7.1-12.3	6.4
pH	N/A	SM4500H	0.01 SU	0.03 SU	8.28	9.5	9.0	8.9-9.2	8.24
Specific conductance	N/A	SM2510	1 umhos/cm	3 umhos/cm	771	713	560	454-460	470

PARAMETER	CAS Number	Test Method	MDL ug/L	LOQ ug/L	Sampling Locations				
					Site 1	Site 2	Site 3	Site 4	Site 5
Turbidity	N/A	SM2130	0.1 NTU	0.3 NTU	5.0	53	29.2	13.7-14.7	15.1
Water temperature	N/A	SM2550	0 ºC	-5 ºC	16.4	25	23.3	24.3	23.3

Fall Creek Flow Data from Gaging Station 03351500 Near Fortville, IN, Downstream from Bridge on State Highway 238.	Sampling Date	Flow (cfs)	Mean Flow (cfs)
* Usual $Q_{7, 10}$ = 15 cfs	9/8/1998 9/9/1998 9/10/1998	46 42 40	43

TABLE 7
Parameter Mean Values & Ranges for Sites 1 - 5

Parameter	Units	Site 1 Mean	Ranges Min/Max		Site 2 Mean	Ranges Min/Max		Site 3 Mean	Ranges Min/Max		Site 4 Mean	Ranges Min/Max		Site 5 Mean	Ranges Min/Max	
Metals																
Aluminum, dissolved	ug	3.45	2.6	4.4	3.1	2.6	3.7	3.5	2.1	4.4	3.5	2.5	5	2.8	1.2	4.1
Aluminum, total recoverable	ug	213	65	326	690	479	860	428	180	670	138	82	220	138	69	230
Antimony, dissolved	ug	0.1	ND	017	0.15	0.12	0.17	0.18	0.14	0.22	0.18	0.15	0.22	0.17	0.15	0.18
Antimony, total recoverable	ug	0.14	0.13	0.16	0.16	0.12	0.19	0.19	0.14	0.25	0.19	0.15	0.24	0.18	0.15	0.22
Arsenic, dissolved	ug	1.4	1.1	1.6	1.7	1.1	1.9	1.8	0.9	2.4	2	1	3.1	1.9	1	3.1
Arsenic, total recoverable	ug	1.6	1.2	1.9	2	1.9	2.1	2.2	1.6	2.4	2.2	1.6	3.1	2.2	1.6	3.2
Beryllium, dissolved	ug	0.04	ND	0.14	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Beryllium, total recoverable	ug	0.006	.005	002	0.03	0.02	0.03	0.01	.005	0.01	ND	ND	ND	ND	ND	ND
Calcium, dissolved	mg	81	80	82	71	50	78	55	49	65	49	42	57	50	42	57
Cadmium, dissolved	ug	0.02	.005	0.03	0.01	.005	0.02	001	.005	0.02	.006	.005	0.01	.006	.005	0.01
Cadmium, total recoverable	ug	0.03	0.02	0.03	0.05	0.04	0.05	0.02	0.01	0.02	0.01	.005	0.02	0.01	.005	0.02
Chromium, dissolved	ug	0.17	0.06	0.26	0.13	0.04	0.23	0.12	0.04	0.17	0.12	0.03	0.17	0.13	0.03	0.15
Chromium, total recoverable	ug	0.92	0.34	2.09	1.48	1.06	2.06	0.53	0.46	1.68	0.46	0.14	1.12	0.32	0.18	0.5
Chromium - III	ug	0.75	<.02	2.09	0.96	<.02	1.9	0.56	<.02	1.6	0.27	<.02	1.07	0.13	<.02	0.49
Chromium - VI, dissolved	ug	0.45	ND	1.1	0.48	ND	1.1	0.25	ND	0.3	0.45	ND	1.1	0.5	ND	1.2
Copper, dissolved	ug	0.76	0.61	0.98	0.94	0.54	1.77	0.68	0.29	0.96	0.7	0.23	1.05	0.71	0.28	1.02
Copper, total recoverable	ug	1.47	0.87	2.07	2.47	1.87	3.18	1.52	1.06	2.18	1.13	0.85	1.46	1.19	0.84	1.52
Iron, dissolved	mg	ND	ND	ND	0.01	ND	0.05	.005	ND	0.01	ND	ND	ND	.004	ND	0.01
Iron, total recoverable	mg	0.38	0.12	06	0.99	0.83	1.2	0.49	0.25	0.76	0.15	0.09	0.23	0.22	0.11	0.36

Parameter	Units	Site 1 Mean	Ranges Min/Max		Site 2 Mean	Ranges Min/Max		Site 3 Mean	Ranges Min/Max		Site 4 Mean	Ranges Min/Max		Site 5 Mean	Ranges Min/Max	
Lead, dissolved	ug	0.15	.016	053	0.05	.016	.091	0.02	ND	.026	0.08	ND	0.312	0.02	0.01	.035
Lead, total recoverable	ug	0.64	0.41	0.81	1.6	1.4	2.3	0.91	0.4	1.3	0.35	0.15	0.83	0.28	0.18	0.47
Magnesium, dissolved	mg	29	27	31	26	17	30	25	23	27	20	19	22	20	18	22
Manganese, dissolved	ug	19	16	22	32	14	58	0.69	0.41	1.1	2.5	0.4	8.7	39	2.8	5
Manganese, total recoverable	ug	36	21	50	76	47	110	52	18	72	36	18	56	32	19	57
Mercury, dissolved	ng	0.34	0.29	04	0.76	0.1	1.84	0.35	0.17	0.57	0.33	ND	0.52	0.61	0.14	1.04
Mercury, total recoverable *	ng	1.18	0.66	20.8	3.3	2	4.5	1.9	1.3	2.9	1.2	0.51	1.71	1.3	0.84	2.3
Nickel, dissolved	ug	2.1	1.6	2.5	2	1.4	2.5	1.6	1.3	1.7	1.3	1.2	1.5	1.5	1.2	1.5
Nickel, total recoverable	ug	3.1	2.6	3.8	3.8	3.1	4.3	2.8	2.2	3.2	2	1.9	2.1	2.0	1.7	2.3
Potassium, dissolved	ug	16	1.6	27	15	1.5	29	13	1.7	20	9.2	2	14	8.8	2	13
Selenium, dissolved	ug	1	0.6	1.3	0.8	0.5	1.3	0.8	0.4	1.4	0.9	0.5	1.2	0.7	0.6	1
Selenium, total recoverable	ug	1.3	0.7	2.1	0.9	06	1.3	1.1	0.7	1.4	1	0.6	1.5	1	0.7	1.2
Silver, dissolved	ug	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Silver, total recoverable	ug	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
Sodium dissolved	ug	5.2	2.1	14	5.8	2.1	15	4.9	2.1	13	4.9	2.3	12	5	2.5	12
Thallium, dissolved	ug	0.018	.015	.035	0.016	0.009	0.029	0.01	ND	0.03	0.009	ND	0.028	0.012	0.004	0.031
Thallium, total recoverable	ug	0.03	.023	.057	0.04	0.031	.066	0.03	0.015	0.052	0.04	0.008	0.046	0.02	0.006	0.051
Zinc, dissolved	ug	0.8	0.6	0.9	.068	0.05	0.08	0.04	0.3	0.5	0.3	0.2	0.5	0.25	0.2	0.3
Zinc, total recoverable	ug	2.6	1.6	3.7	6.1	5.2	8	2.9	1.8	4.2	0.9	0.6	1.1	1.1	0.8	1.6
NON-METAL PARAMETERS																
Alkalinity, dissolved	mg	274	245	274	233	162	265	196	188	204	172	163	181	175		180
Chloride, dissolved	mg	40	30	51	37	22	56	34	28	41	26	22	29	25	165	29

Parameter	Units	Site 1 Mean	Ranges Min/Max		Site 2 Mean	Ranges Min/Max		Site 3 Mean	Ranges Min/Max		Site 4 Mean	Ranges Min/Max		Site 5 Mean	Ranges Min/Max	
Hardness (as $CaCO_3$)	mg	327	320	330	277	200	320	233	230	240	203	200	210	207	200	210
Nitrogen, nitrate, dissolved	mg	2.1	ND	3.68	2.5	1.4	3.5	0.99	0.87	2.97	0.96	0.31	2.4	1.2	0.54	2.3
Nitrogen, total (TKN), dissolved	mg	0.29	0.2	0.4	0.43	0.02	0.64	0.41	0.28	0.64	0.5	0..34	0.66	0.38	ND	0.57
Organic carbon, dissolved (DOC)	mg	2.4	2.2	2.7	3.4	2.5	5.1	3.1	3	3.2	3.7	3.6	3.7	3.7	3.5	4
Phosphorus, total, dissolved	mg	0.05	0.03	0.08	.054	0.03	0.08	001	.009	.012	0.01	.009	.012	0.01	.009	.013
Solids, filterable residue (TDS)	mg	435	406	456	392	290	458	326	308	348	279	260	316	285	262	320
Solids, total residue (TS)	mg	491	458	524	465	370	516	387	360	416	321	302	340	332	308	340
Sulfate, dissolved	mg	57	43	66	48	35	61	44	36	46	34	31	35	33	30	34
Suspended particulate matter (SPM)	mg	9.3	1.1	22	23.2	16	32	17.6	10	22	6.3	2	8.9	8.3	1.4	12
HYDROLAB PARAMETERS																
Dissolved oxygen (DO)	mg	8.9	7.9	10.6	9.9	7.3	13.9	11.4	6.05	14.0	7.1 - 11.5	4.0	15.4	7.83	6.4	9.6
pH	SU	8.4	8.3	8.4	8.6	8.2	9.5	8.8	8.7	9.0	8.5 - 8.1	8.1	9.2	8.5	8.3	8.9
Specific conductance	umhos/ cm	714	634	771	629	468	713	545	522	562	465 - 475	454	491	481	470	490
Turbidity	NTU	5.7	1.4	10.8	46	38.9	53	39.5	29	49	9.3 - 15.2	9.5	18.8	8.1	5.8	15
Water temperature	C	19.6	16.4	24	22.9	15.2	26.7	23.6	15.6	27.8	16.5 - 24.6	14.8	27.8	23.5	17.4	27.2

* The Total Mercury results for the May sampling event for site 1 were 10 times higher than any other sample results in this study (see Tables 3-6). Therefore, the Total Mercury results from May sampling event #1 were not included in the mean calculations. The mean value for each parameter for each sampling site or location was obtained from data collected in four sampling events conducted in May, July, August and September 1998.

minimum and maximum total recoverable metal concentrations for the four metals were: **Aluminum 65 & 860 ug/L; Lead 0.15 & 2.3 ug/L**; **Mercury 0.00051 & 0.0045 ug/L (0.51-4.5 ng/L)**; and **Zinc 0.6 & 6.1 ug/L**. (see **Table 7**).

As compared to Aluminum, Lead, Mercury and Zinc, four other metals (**Arsenic, Cadmium, Copper, Nickel, and Selenium**) showed less differences between dissolved and total recoverable metals, but as expected for each of these metals total recoverable metal concentrations were relatively higher than the dissolved metal (see **Table 7**). The minimum and maximum total metal concentrations for each of these metals were **Arsenic 1.2 & 3.2 ug/L**; **Cadmium 0.005 ug/L & 0.05 ug/L, Copper 0.84 ug/L & 3.18 ug/L**, **Nickel 1.7 & 4.3 ug/L, and Selenium 0.6 ug/L & 2.1 ug/L**. The minimum and maximum dissolved metal concentrations for each of these metals were **Arsenic 0.9 & 3.1 ug/L**; **Cadmium 0.005 ug/L & 0.03 ug/L, Copper 0.23 ug/L & 1.77 ug/L**, **Nickel 1.2 & 2.5 ug/L, and Selenium 0.4 ug/L & 1.4 ug/L**.

Except for Aluminum, as discussed above, no other metals were present in significant amounts in the ambient water in the Fall Creek. At all five sampling locations Aluminum was mostly present as total recoverable metal (**65 ug/L as minimum and 860 ug/L as maximum**), but the dissolved metal concentrations for Aluminum were extremely low (**1.2 ug/L as minimum and 4.4 ug/L as maximum**), see **Table 7**.

Non-Metals and Hydrolab Parameters:

Analytical results for conventional chemistries obtained in the lab, and/or in the field using the Hydrolab from all 5 sampling locations from each sampling event were unremarkable: a) **Alkalinity**, **Chloride**, **Total Nitrogen**, **Nitrites (**measured as dissolved nitrogen), **DOC**, **Phosphorous**, **TDS**, **TS**, **Sulfate**, **pH**, **Specific Conductance,** etc., were all within acceptable range; b) Suspended Particulate Matter (SPM) was also present in very small amounts at all 5 locations (2 mg/L as minimum to 32 mg/L as maximum); and c) Hardness of the water in Fall Creek ranged from **200 mg/L** to **330 mg/L** as $CaCO_3$ at all locations, see **Tables 3 to 6** and **Table 7.**

Comparison of Metal Concentrations with WQC and Fixed Station Data:

Arithmetic Grand Mean Concentrations for each metal parameter from all 5 sampling locations were calculated & compared with the available chronic WQC or standards. For outside the Great Lakes Basin WQC are expressed as total recoverable metals only. Therefore, the dissolved metal WQC for eight metals (**Arsenic, Cadmium, Chromium III, & VI, Copper, Lead, Nickel, and Zinc**) were obtained by multiplying the aquatic chronic WQC for total recoverable metals by the **Metal Translator** (or the **Conversion Factor**) for the individual metal. Except for Arsenic, the WQC for **Cadmium**, **Chromium III**, **Copper**, **Lead**, **Nickel**, and **Zinc** are based on water hardness. Therefore, the WQC for these six metals at Fall Creek mean hardness value of **250 mg/L as CaCO3** were used to obtain the dissolved metal criteria. A complete listing of all the metal data & its comparison with the total and dissolved metal WQC criteria is provided in **Table 8**.

TABLE 8
Comparison of Metal Concentrations in Fall Creek with Water Quality Criteria (WQC) & Fixed Station Data

		WQC			Comparison with Fixed Station Data							
Parameter	Units	Water Quality Criteria Total (Chronic)	Water Quality Criteria Dissolved (Chronic)	Grand Mean Total #	May Site 1-5 Mean	FS May FC 0.6	July Site 1-5 Mean	FS July FC 0.6	Aug Site 1-5 Mean	FS Aug FC 0.6	Sept Site 1-5 Mean	FS Sept FC 0.6
METAL PARAMETERS												
Aluminum, total recoverable	ug	174 @	---	321	227		377		298		383	
Antimony, total recoverable	ug	30	---	0.17	0.14		0.17		0.17		.21	
Arsenic, total recoverable	ug	190	190	2.04	1.8	< 2	1.98	< 2	2	< 2	2.5	< 2
Beryllium, total recoverable	ug	1.17		0.01	0.014		0.01		0.01		.01	
Cadmium, total recoverable	ug	2.3 *	2.07 *	0.02	0.02	< 0.9	0.02	< 0.9	0.02	< 0.9	.03	< 0.9
Chromium, total recoverable	ug	438		0.74	0.58	< 5	1.49	< 5	0.47	< 5	.66	10
Chromium - III	ug	438*	377 *	0.54	0.34		1.43	0.47	0.4		< 0.2	
Chromium - VI, dissolved	ug	11	10.6	0.43	0.24		ND		ND		.96	
Copper, total recoverable	ug	26 *	25 *	1.56	1.81	< 4	1.92	7	1.31	< 4	1.17	< 4
Iron, total recoverable	mg	1		0.45	0.38	.74	0.48	0.61	0.42	.31	.41	.35
Lead, total recoverable	ug	10 *	7.9 *	0.76	0.60	< 6	0.68	< 6	0.62	< 6	1.13	10
Manganese, total recoverable	ug	---		46.4	32.8		43		46.8		61.8	
Mercury, total recoverable ●	ng	12		1.7	1.42	100	2.2	< 0.1	1.27	< 100	2.23	< 100
Nickel, total recoverable	ug	342 *	341 *	2.74	2.3	< 6	2.9	6.2	2.89	< 6	2.82	< 6
Selenium, total recoverable	ug	35		1.1	1.4		1.2		0.86		.66	
Silver, total recoverable	ug	0.12 *		ND	ND		ND		ND		ND	

		WQC			Comparison with Fixed Station Data							
Parameter	Units	Water Quality Criteria Total (Chronic)	Water Quality Criteria Dissolved (Chronic)	Grand Mean Total #	May Site 1-5 Mean	FS May FC 0.6	July Site 1-5 Mean	FS July FC 0.6	Aug Site 1-5 Mean	FS Aug FC 0.6	Sept Site 1-5 Mean	FS Sept FC 0.6
Thallium, total recoverable	ug	40		0.03	0.05		0.035		0.019		.02	
Zinc, total recoverable	ug	230 *	227 *	2.7	2.6	5.1	2.63	13	2.52	< 4.5	3.05	< 4.5
NON-METAL PARAMETERS												
Alkalinity, dissolved	mg	20		208	170		200		199		209	
Chloride, dissolved	mg	230		32	28.7		27.6		31.4		41.4	
Hardness (as $CaCO_3$)	mg	120-5000		249			238		254		256	
Nitrogen, nitrate,dissolved	mg	10		1.6	2.96		1.82		0.48		.85	
Nitrogen, total (TKN), dissolved	mg	0.1		0.40	0.28		0.48		0.45		.37	
Organic carbon, dissolved (DOC)	mg	----		3.26			3.6		3.14		3.02	
Phosphorus, dissolved	mg	0.03		0.03	0.02		0.03		0.03		.03	
Solids, filterable residue (TDS)	mg	750		343	360		325		334		354	
Solids, total residue (TS)	mg	----		399	392		391		416		396	
Sulfate, dissolved	mg	250		43	37.8		40.5		45.4		48	
Suspended particulate matter (SPM)	mg	---		12.9	14.9		9.8		13.1		13.9	
HYDROLAB PARAMETERS												
Dissolved oxygen (DO)	mg	≥ 5		9.5	11		7.2		9.6		10.1	
pH	SU	6-9		8.6	8.6		8.4		8.5		8.8	

		WQC			Comparison with Fixed Station Data							
Parameter	Units	Water Quality Criteria Total (Chronic)	Water Quality Criteria Dissolved (Chronic)	Grand Mean Total #	May Site 1-5 Mean	FS May FC 0.6	July Site 1-5 Mean	FS July FC 0.6	Aug Site 1-5 Mean	FS Aug FC 0.6	Sept Site 1-5 Mean	FS Sept FC 0.6
Specific conductance	umhos/ cm	1,200		568	550		548		578		503	
Turbidity	NTU	50		22.3			24.5		17.2		23.3	
Water temperature	C	10-32.2		22.0	15.9		26.6		25.8		22.5	

● From Site 1 the Total Mercury results for the May sampling event were 10 times higher than any other sample results in this study (see Tables 3-6). Therefore, Total Mercury results from May sampling event #1 for site 1 were not included in the Grand Mean or Mean Calculations.

@ Water Quality Criterion(WQC) for aluminum is lowered from the calculated site-specific chronic criterion value of 993 ng/L to protect striped bass and other surrogate species in outside the Great Lakes Basin. In the 1998 EPA Criteria document for aluminum, the calculated chronic WQC for aluminum is 748 ng/L, but this was lowered to 87 MDL to protect brook trout and striped bass fish.

* Water Quality Criteria (WQC) for these metals are based on water hardness equivalent to 250 mg/L $CaCO_3$.

\# To compare with WQC, the Grand Mean of each parameter and total metal concentration was obtained from all the five sampling sites or locations in Fall Creek sampled at four different occasions in May, July, August, and September 1998.

It is interesting to note that, except for aluminum, concentration of each total or dissolved metal was lower than the chronic WQC for the same metal in Fall Creek. The chronic WQC for aluminum is **993 ug/L** as calculated by IDEM, (or **748 ug/L** as calculated by EPA and **87 mg/L** as adjusted by EPA to protect salmonid and striped bass), but it was adjusted by IDEM to **174 ug/L** to protect striped bass. Concentrations of total aluminum in Fall Creek at all sampling locations were found to exceed the **174 ug/L**. However at all the five sampling locations, concentrations of dissolved aluminum were very low and ranged from **1.2 ug/L as minimum to 4.4 ug/L as maximum** (see **Table 7 and Table 8**). It appears that aluminum is mostly bound to particulate matter and may not be bioavailable for toxicity to aquatic life. Since the dissolved aluminum concentrations in Fall Creek are extremely low, therefore, presence of total aluminum in high concentrations in the Fall Creek should not be of great concern.

Data from the trace metal pilot project was also compared with the conventional metal data from a Fall Creek Fixed Station Site **(FC 0.6)** collected in the same months in **May**, **July**, **August** & **September 1998** (see **Table 8**). The Fixed Station Site is located at Stadium Drive Bridge which is downstream from the 5 sampling sites (See **Figure 1**). **Table 8** contains the **Water Quality Criteria** for individual metal or non-metal parameter and the **Grand Mean** for each parameter from all the five sampling locations from four sampling events in May, July, August and September 1998. **Table 8** also contains both the **Monthly Mean Values** for individual metal or non-metal parameters from five sampling sites and the monthly results from a Fall Creek Fixed Station Site (FC 0.6) located at Stadium Drive Bridge for the months of May, July, August, and September 1998. As expected, for the Fixed Station data the traditional reporting limits were too high for most of the parameters to identify the true metal concentrations. The Fixed Station metals data also show that the total **cadmium, chromium**, **copper, lead**, **mercury, nickel,** and **zinc** concentrations were at least 5 to 10 times higher than the same metal concentrations obtained by using Ultra-Clean Techniques for sampling & analysis of ambient waters. The high metal concentration noticed in the Fixed Station data may be due to conventional methods used for sampling and analysis of ambient waters.

Quality Assurance Measurements:

a. In-Lab Data Quality Assurance:

Precision: The in-lab data quality assurance for analytical **Precision** was based on laboratory Duplicates, Matrix Spike Duplicates and Relative Percent Difference (RPD). Except for a few variations the overall precision average RPD for all the analyses was acceptable at 4.8%, which was well within the 0% - 20% required criteria limits (see **Table 9 and Table 10**).

Accuracy: The in-lab analytical accuracy was based on matrix spikes, matrix spike duplicates, quality control samples, and on-going performance recovery samples. The overall % recovery was 100% which was well within the 90% to 110% (see **Table 11**) acceptable range. The analytical performance for this project as evidenced by both precision and accuracy in the WSLH analytical laboratory demonstrates that analytical data generated for this project is very precise and could be used for any regulatory or water quality management decisions.

TABLE 9
Results of Quality Control Samples

	Tubing Blank				Source Blank				Filter Blank				Duplicate RPD				MS / % RPD of MS/MSD			
PARAMETER	**M**	**J**	**A**	**S**	**M**	**J**	**A**	**S**	**M**	**J**	**A**	**S**	**M**	**J**	**A**	**S**	**May**	**July**	**Aug**	**Sept**
METALS																				
Aluminum, dissolved									0.1	0.2	ND	ND	3	4	40	16	94/0.4	96/3	107/5	100/1
Aluminum, total recoverable	0.9	0.4	ND	ND	0.5	0.3	ND	ND					3	15	6	0	102/1		99/1	98/1
Antimony, dissolved					ND				ND	ND	ND	ND	1	6	0	5	104/.2	101/1	102/-	104/2
Antimony, total recoverable	0.01	ND	ND	ND		ND	ND	ND					3	0	5	4	98/2	102/2	101/2	97/1
Arsenic, dissolved									ND	ND	ND	ND	1	0	0	3	105/.3	107/.4	105/-	115/.3
Arsenic, total recoverable	ND	ND	ND	ND		ND	ND	ND					3	0	0	0	107/.5	107/2	97/4	113/1
Beryllium, dissolved									ND	ND	ND	ND	ND	ND	ND	ND	101/0	91/.5	94/-	86/.3
Beryllium, total recoverable	ND	ND	ND	ND	ND	ND	ND	ND					5	ND	ND	ND	103/1	95/2	90/.3	90/2
Calcium, dissolved									ND	ND	ND	ND		0	0	0	105/-	98/-	91/-	94/-
Cadmium, dissolved									ND	ND	ND	ND	ND	ND	ND	0	104/1	99/1	100/-	100/.1
Cadmium, total recoverable	ND	ND	ND	ND	ND	ND	ND	ND					5	ND	0	0	102/0	100/.1	103/1	87/1
Chromium, dissolved	0.2								0.04	.06	ND	ND	8	20	0	86	103/5	106/1	115/2	104/3
Chromium, total recoverable	0.04	0.15	ND	ND	0.05	0.11	ND	0.02					6	12	0	8	96/3	127/2	98/2	100/1

PARAMETER	Tubing Blank				Source Blank				Filter Blank				Duplicate RPD				MS / % RPD of MS/MSD			
	M	J	A	S	M	J	A	S	M	J	A	S	M	J	A	S	May	July	Aug	Sept
Chromium - III*	<0.2	ND	<0.2	<0.2	<0.2	ND	<0.2	<.2	<.2	ND	<.2			5	ND	0				
Chromium - VI, dissolved	0.2	ND	ND	1.3	0.2	ND	ND	0.4	<.5	ND	ND	.3	ND	ND	ND	28	97/0	98/1	95/-	105/.3
Copper, dissolved					0.06				ND	0.05	ND	ND	0.3	18	6	7	96/1	101/1	100	94/1
Copper, total recoverable	0.04	ND	ND	ND		ND	ND	ND					2	6	3	4	104/3	105/.3	96/1	95/.2
Iron dissolved									ND	ND	ND	ND	2	ND	ND	ND	99/-	101/-	96/-	97/-
Iron, total recoverable	ND	ND	ND	ND	ND	ND	ND	ND					2	0	8	0	100/-		97/-	98/-
Lead, dissolved										ND	ND	ND	2	167	25	ND	110/.4	103/.3	100	102/1
Lead, total recoverable	0.005	ND	ND	ND	ND	ND		0.02					1	2	4	7	103/.3	103/.2	101/1	99/2
Magnesium, dissolved										ND	ND	ND	1	0	5	0	103/-	101/-	97/-	97/-
Manganese, dissolved									ND	0.02	ND	ND	2	2	3	1	103/.1	98/1	94/-	97/.2
Manganese, total recoverable	ND	ND	ND	0.01		ND	ND	ND	0.01				1	5	3	2	107/-		99/-	99/-
Mercury, dissolved										ND	ND	ND	17	81	ND	22		91/-	98/-	104/-
Mercury, total recoverable	<0.1	.38	0.12	ND	<0.1	ND	0.1	ND	0.1					21	10	8	92/-	99/-	116/-	108/-
Nickel, dissolved									ND	ND	ND	ND	5	36	0	2	100/2	77/0	92/-	93/7
Nickel, total recoverable	ND	ND	ND	ND	0.17	ND	ND	ND					4	12	1	4	97/1	103/1	102/2	104/.5
Potassium, dissolved									ND	ND	ND	ND	3	1	0	0	102/-	100/-	98/-	101/-

PARAMETER	Tubing Blank M	Tubing Blank J	Tubing Blank A	Tubing Blank S	Source Blank M	Source Blank J	Source Blank A	Source Blank S	Filter Blank M	Filter Blank J	Filter Blank A	Filter Blank S	Duplicate RPD M	Duplicate RPD J	Duplicate RPD A	Duplicate RPD S	MS / % RPD of MS/MSD May	July	Aug	Sept
Selenium, dissolved									.3	ND	ND	ND	ND	0	18	15	117/-	112/4	108/5	110/2
Selenium, total recoverable	ND	ND	ND	ND	0.4	ND	ND	ND					8	40	12	15	111/4	117/2	93/5	85/0
Silver, dissolved									ND	ND	ND	ND	ND	ND	ND	ND	97/1	100/.5	95.3/-	92/.1
Silver, total recoverable	ND	0.01	ND	ND	ND	0.01	ND					ND	ND	ND	ND	ND	98/-	102/2	96/.2	95/.1
Sodium dissolved									ND	0.02	ND	ND	2	2	0	4	104/-	104/-	96/-	98/-
Thallium, dissolved									ND	ND	ND	ND	0	40	ND	0	111/.2	107/.3	106/3	101/4
Thallium, total recoverable	ND	ND	ND	ND	ND	0.004	0.004	ND					1	53	73	0.006	104/1	106/.4	101/2	94/.5
Zinc, dissolved									0.05	ND	ND	ND	4	17	23	0	106/3	95/0.1		99/-
Zinc, total recoverable	ND	ND	ND	ND	ND	ND	ND	ND					0.3	2	1	2	104/-	95/1	86/2	97/2
NON-METAL PARAMETERS																				
Alkalinity, dissolved	<1				1		<1	3	1		2		0.2	0	0	0				
Chloride, dissolved	ND				ND		0.4	ND	ND		0.6		7	.5	4	0.3				
Hardness (as $CaCO_3$)										ND	ND	ND		0	0	0				
Nitrogen, nitrate, dissolved	0.47				0.28		1.76	ND	0.26		0.3		1	1	6	0		104		
Nitrogen, total (TKN), dissolved					ND				ND		ND	ND	0	5	0	2		110	99	105

PARAMETER	Tubing Blank				Source Blank				Filter Blank				Duplicate RPD				MS / % RPD of MS/MSD *			
	M	J	A	S	M	J	A	S	M	J	A	S	M	J	A	S	May	July	Aug	Sept
Organic carbon, dissolved (DOC)											0.4	ND		5	6	3				
Phosphorus, total, dissolved											ND	ND		8	11	15		102	101	98
Solids, filterable residue (TDS)							ND				ND	ND	3	1	0	0				
Solids, total residue (TS)							ND	ND						3	2	1				
Sulfate, dissolved	0.1				0.1		ND	ND	0.13		ND		4	0.7	0	0		109		106
Suspended particulate matter (SPM)							.23	0.09						101	1	19				
HYDROLAB PARAMETERS																				
Dissolved oxygen (DO)																				
pH	4.49				4.73		4	5.64	4.72		4.86			0	0	0.4				
Specific conductance	16				10		53	2	10		8			0.2	0.2	0.2				
Turbidity																				
Water temperature																				

Note: M = May, J = July, A = August, S = September.

* Relative Percent Difference (%RPD) is shown by a slash.

TABLE 10
Precision Based on In-Lab Duplicates & Matrix Spike :
Expressed as Relative Percent Difference (RPD)

	Sampling Events				
	May-98	Jul-98	Aug-98	Sep-98	
Parameter	Average RPD	Average RPD	Average RPD	Average RPD	Study Average RPD
Overall Precision	5.0	6.3	4	3.8	4.8
Dissolved Metals and Non-Metals	2.6	8.1	3.7	4.3	4.7
Total Metals and Non-Metals	8.0	1.7	3.0	3.9	4.2

TABLE 11
Accuracy Assessment Based on In-lab Analysis of
Quality Control Samples and Ongoing
Precision and Percent Recovery

	Sampling Events				
	May-98	Jul-98	Aug-98	Sep-98	
Parameter	% Recovery	% Recovery	% Recovery	% Recovery	Study Average Recovery
Overall Accuracy	99.8	102.3	100.2	100.1	100.6
Accuracy Metals and Non-Metals	102.5	102.6	100.1	100.0	101.3

However, a few anomalies were noted. A mercury contamination was found in one of the in-lab processing blanks only and therefore should cause no effect on the data and does not demonstrate a field sampling error.

Holding time was exceeded by 1 or 2 days in a few samples (Dissolved Chloride, Dissolved Sulfate, TDS, OC, TDS) but the exceedance was not excessive and will not have an effect on the data.

b. In-Field Data Quality Assurance:

Field data quality of field sampling techniques were monitored with the equipment or source blanks and field duplicates. The quality control data summarized in **Table 9**, showed that the overall precision expressed as Relative Percent Difference of the field duplicates was 10.1 %. (see **Table 12**)

With some of the metal parameters (**Total Aluminum, Total & Dissolved Chromium, Chromium VI, Total & Dissolved Copper, Total Nickel, Total Lead, Total Mercury, Total Selenium, Total Silver, and Total Thallium**) there were some contaminations found in the blanks (see **Table 9**). But in some instances the results were very close to the reporting limits and did not significantly effect the results. Due to significant contamination found in the **Blanks** (B) ten of the reported blank contaminations resulted in flagging results as ‘J’ (estimated). These estimated results effected by contaminations in the blank were biased high. This also means that the actual results summarized in **Tables 3** to **6** for the indicated parameters: Nitrate (5/98 & 8/98), Nickel (9/98), Chromium (7/98), Mercury(7/98), Hex. Chromium(9/98) could be slightly lower than the listed results.

c. Completeness:

The percent completeness goal for the trace project was set at 80% for field work and at or above 95% for laboratory analysis and data collection.

Originally three sampling events were planned, but in reality four sampling events were conducted. At each of the sampling events several water samples for numerous parameters were collected and thereby accomplished greater than 80% of completeness goal for field work.

In the laboratory, analysis of all the water samples was completed from each sampling event. Although analysis work was delayed because of instrumental problems, but this did not effect the overall performance and analysis of the water samples for all the parameter selected. The completeness for analysis of all the water samples & all the parameters was 100% and thereby far exceeded the 95% completeness goal for laboratory analysis.

d. Data Quality Assessments (DQAs):

As per the QAPP for the Trace Metal Pilot Project the **DQA** for this project was set at **Level 2** for the field work and **DQA Levels 3** for the Laboratory data. A complete listing of **4 DQA** & full description of each DQA level is written below. A check mark ( ) below indicates the DQA Level to which the analytical data qualifies.

TABLE 12

Precision Based on Field Duplicates:
Expressed as Relative Percent Difference

	Sampling Events			
	May-98	Jul-98	Sep-98	
Parameter	Average RPD	Average RPD	Average RPD	Study Average RPD
Overall Accuracy	16.9	6.9	6.4	10.1
Dissolved Metals and Non Metals	29.7	9.0	11.2	16.6
Total Metals and Non Metals	13.0	8.0	3.9	8.3

Level 1 Screening data: The results are usually generated onsite and have no QC checks. Analytical results, which have no QC checks or no precision or accuracy information or no detection limit calculations, but just numbers, are included in this category. Primarily, onsite data are used for presurveys and for preliminary rapid assessment.

Level 2 [ ] **Field analysis data:** Data is recorded in the field or laboratory on calibrated or standardized equipment. Field duplicates are measured on a regular periodic basis. Calculations may be done in the field or later at the office. Analytical results, which have limited QC checks, are included in this category. Detection limits and ranges have been set for each analysis. The QC checks information for field or laboratory results is useable for estimating precision, accuracy, and completeness for the project. Data from this category is used independently for rapid assessment and preliminary decisions.

Level 3 [ ] **Laboratory analytical data:** Analytical results include QC check samples for each batch of samples from which precision, accuracy, and completeness can be determined. Detection limits have been determined using 40 CFR Part 136 Appendix B, Revision 1.11. Raw data, chromatograms, spectrograms, and bench sheets are not included as part of the analytical report, but are maintained by the Contract Laboratory for easy retrieval and review. Data can be elevated from level 3 to level 4 by the inclusion of this information in the report. In addition, level 4 QC data must be reported using CLP forms or CLP format. Data falling under this category is considered as complete and is used for regulatory decisions.

Level 4 Enforcement data: *Analytical results mostly meet the USEPA required Contract Laboratory Program (CLP) data analysis, contract required quantification limits (CRQL), and validation procedures.* QC data is reported on CLP forms or CLP format. Raw data, chromatograms, spectrograms, and bench sheets are included as part of the analytical report. Additionally, all reporting information required in the IDEM/BAA and in the Surface Water QAPP Table 11-1 are included. Data is legally quantitative in value, and is used for regulatory decisions.

e. Comment:

The analytical results received from WSLH meet DQA Level 3 and results of analysis for the Hydrolab field data meet DQA Level 2, and both DQA levels are acceptable for OWM decision making.

f. Compliance Statement:

The laboratory results for surface water samples received fromWisconsin State Laboratory of Hygiene (WSLH), were reviewed for compliance with IDEM BAA 97-44, dated 4/18/97 and OWM DRAFT Quality Assurance Project Plan (QAPP), Rev. 0, for Trace Metal Pilot Project.

DISCUSSION

This Trace Metal Pilot Project study was designed to develop expertise in "**Clean Sampling Techniques**" in order to collect and analyze ambient water samples for dissolved and total recoverable metals using **Ultra-Clean Techniques** at trace levels and compare them mainly with the water quality standards that are based on dissolved or total recoverable metals. This project was funded through a **Federal Grant CP 985282-01, USEPA Section 104 (b)(3)**.

IDEM contracted the **Wisconsin State Laboratory of Hygiene (WSLH)** to provide surface water analysis for metals using **Inductively Coupled Plasma Mass Spectrometry (ICP/MS)** and several other parameters analysis by conventional methods. As part of the scope of work for this project, WSLH staff provided initial training and assistance to the IDEM staff on collecting samples using clean sampling techniques. The WSLH staff also designed and built much of the sampling equipment that were used by the IDEM staff for sampling of ambient waters. The WSLH also supplied pre-cleaned sampling bottles, preservatives and other necessary equipment to IDEM prior to each sampling event. In all, **May through Sept 1998,** four sampling events were conducted. In the first sampling event, WSLH staff trained IDEM staff, while the 3 other sampling events were conducted exclusively by IDEM staff.

Among the several metals, a total of ten metals **(Aluminum, Arsenic, Cadmium, Chromium III, Copper, Lead, Mercury, Nickel, Selenium, and Zinc**) were predominant and were detected at all the five sampling sites (see **Tables 3 thru 6** and **Figures 5 thru 14**). The difference between dissolved and total metals concentrations is shown in the respective figure for each metal. The data show that the difference between total and dissolved metals concentrations was greater with **Aluminum, Lead, Mercury and Zinc** (see **Figures 5,10, 11, & 14**), while the six other metals (**Arsenic, Cadmium, Chromium, Copper, Nickel, and Selenium**) showed less difference between dissolved and total metals concentrations (see **Table 3** thru **6** and **Figures 6, 7, 8, 9**, **12**, and **13**).

Comparison of the metals data with the water quality standards showed that the dissolved metals and even the particulate or total metal concentration for each metal was lower than the lowest WQS for the individual metal (see **Table 8** and **Figures 5** thru **14**). For outside the Great Lakes region dissolved WQC are not available. Therefore, the dissolved WQC were obtained for **Arsenic, Cadmium, Chromium (III & VI), Copper, Lead, Nickel, Selenium, and Zinc** using metal translators or conversion factors developed by USEPA (1996). Comparison of dissolved metal concentration found in Fall Creek at five locations with the dissolved metal WQC are shown in **Table 8** and **Figures 5** thru **14**. In each case, the dissolved metal concentration in ambient water was lower than the calculated dissolved metal WQC for the same metal. Likewise, the total metal concentration for each metal were found to be lower than the respective WQC for individual metal.

At each sampling location and in each water sample, each metal was positively detected as both total and dissolved metals. And not even in one case, concentration of any metal was below the quantitation limit (3 x MDL). This was made possible, because of the clean sampling techniques and the, low detect ultra- Clean ICP/MS analytical methods that were used in this pilot project. In the absence of such analytical methods, and if the conventional methods were used for analysis, dissolved metal concentrations would have turned up as below detection limits and this would have lead to several

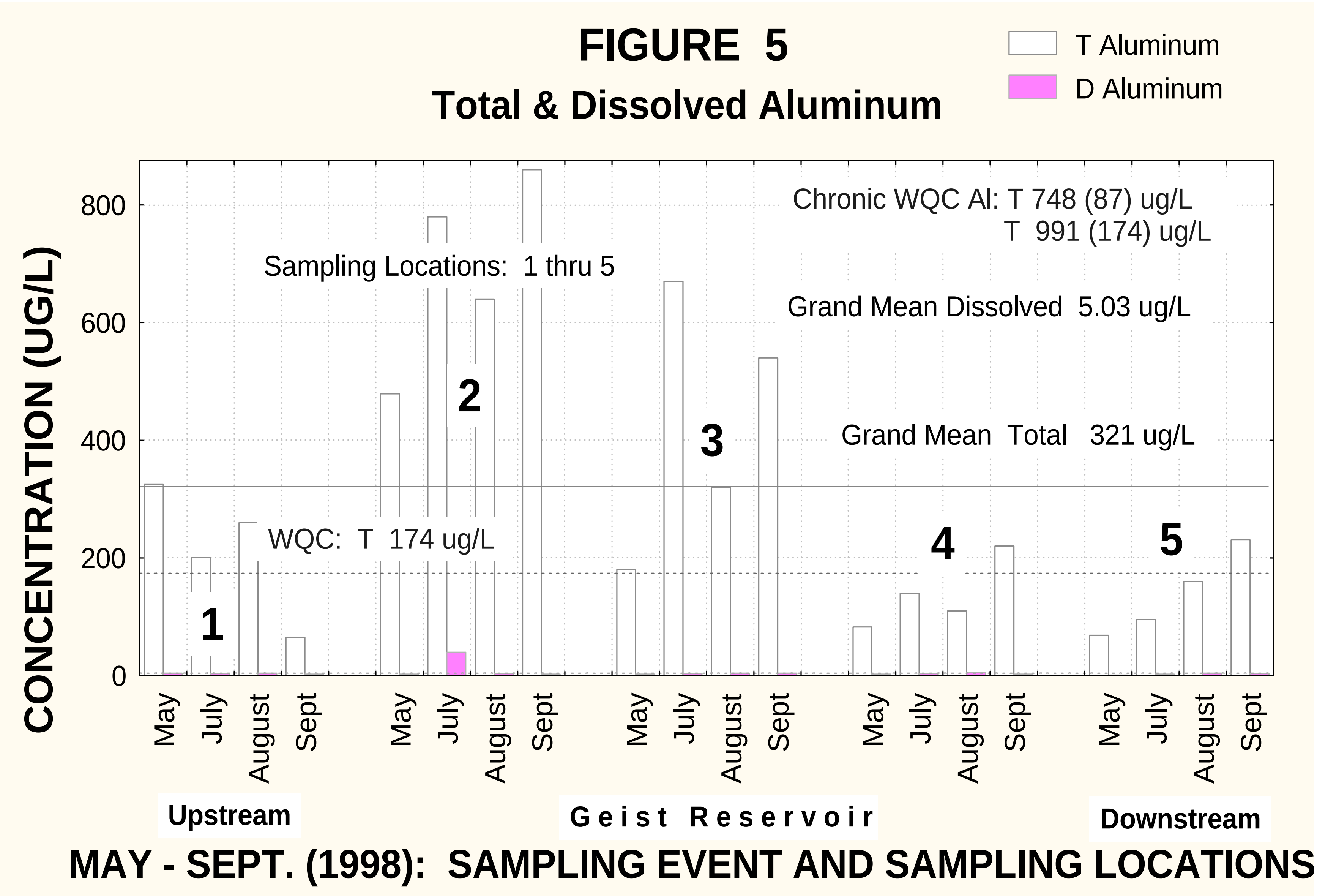


FIGURE 5
Total & Dissolved Aluminum
T Aluminum
D Aluminum
CONCENTRATION (UG/L)
0
200
400
600
800
Chronic WQC Al: T 748 (87) ug/L
T 991 (174) ug/L
Sampling Locations: 1 thru 5
Grand Mean Dissolved 5.03 ug/L
Grand Mean Total 321 ug/L
WQC: T 174 ug/L
1
2
3
4
5
May
July
August
Sept
Upstream
Geist Reservoir
Downstream
MAY - SEPT. (1998): SAMPLING EVENT AND SAMPLING LOCATIONS

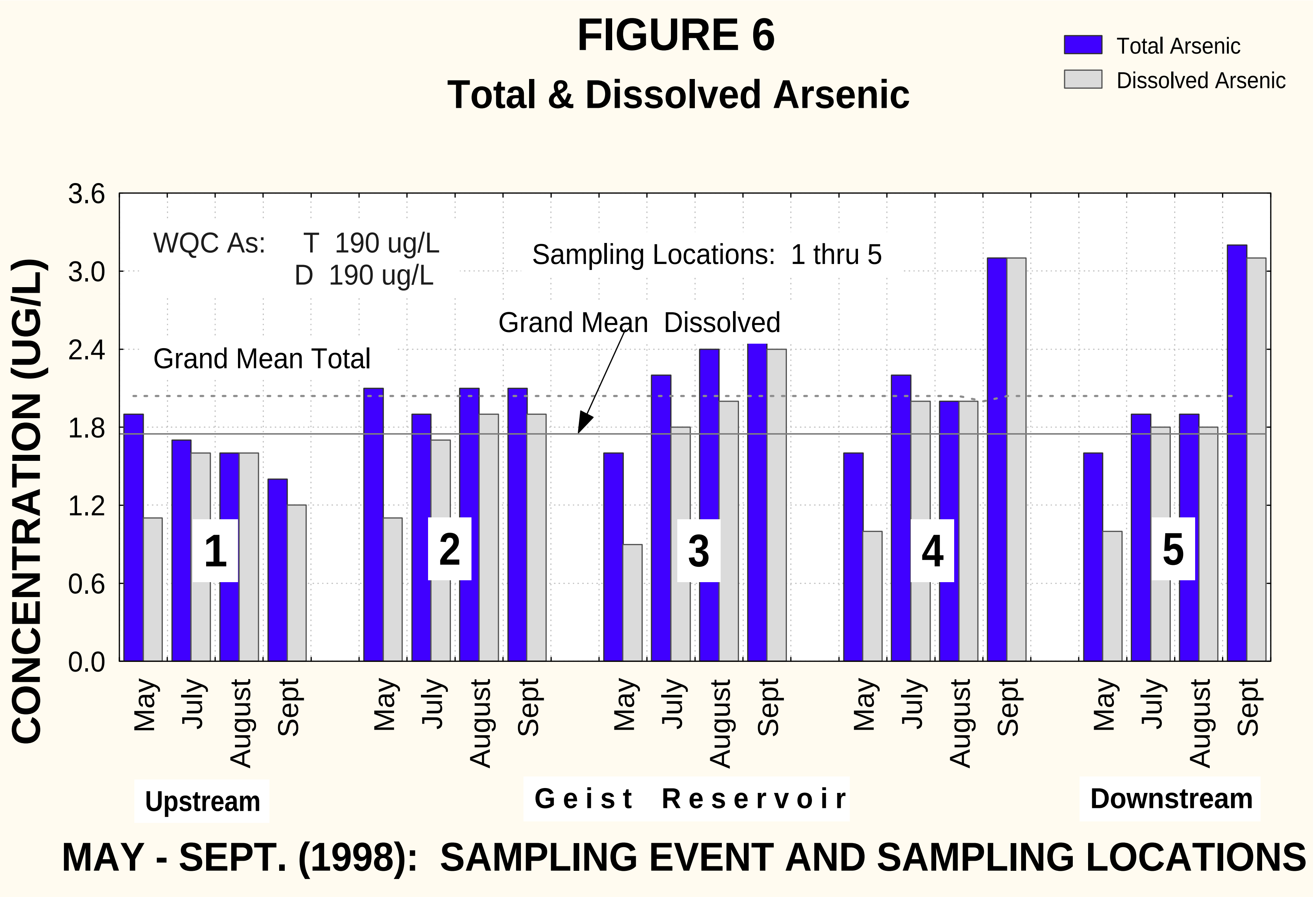


FIGURE 6
Total & Dissolved Arsenic
Total Arsenic
Dissolved Arsenic
CONCENTRATION (UG/L)
3.6
3.0
2.4
1.8
1.2
0.6
0.0
WQC As: T 190 ug/L
D 190 ug/L
Sampling Locations: 1 thru 5
Grand Mean Dissolved
Grand Mean Total
1
2
3
4
5
May
July
August
Sept
Upstream
Geist Reservoir
Downstream
MAY - SEPT. (1998): SAMPLING EVENT AND SAMPLING LOCATIONS

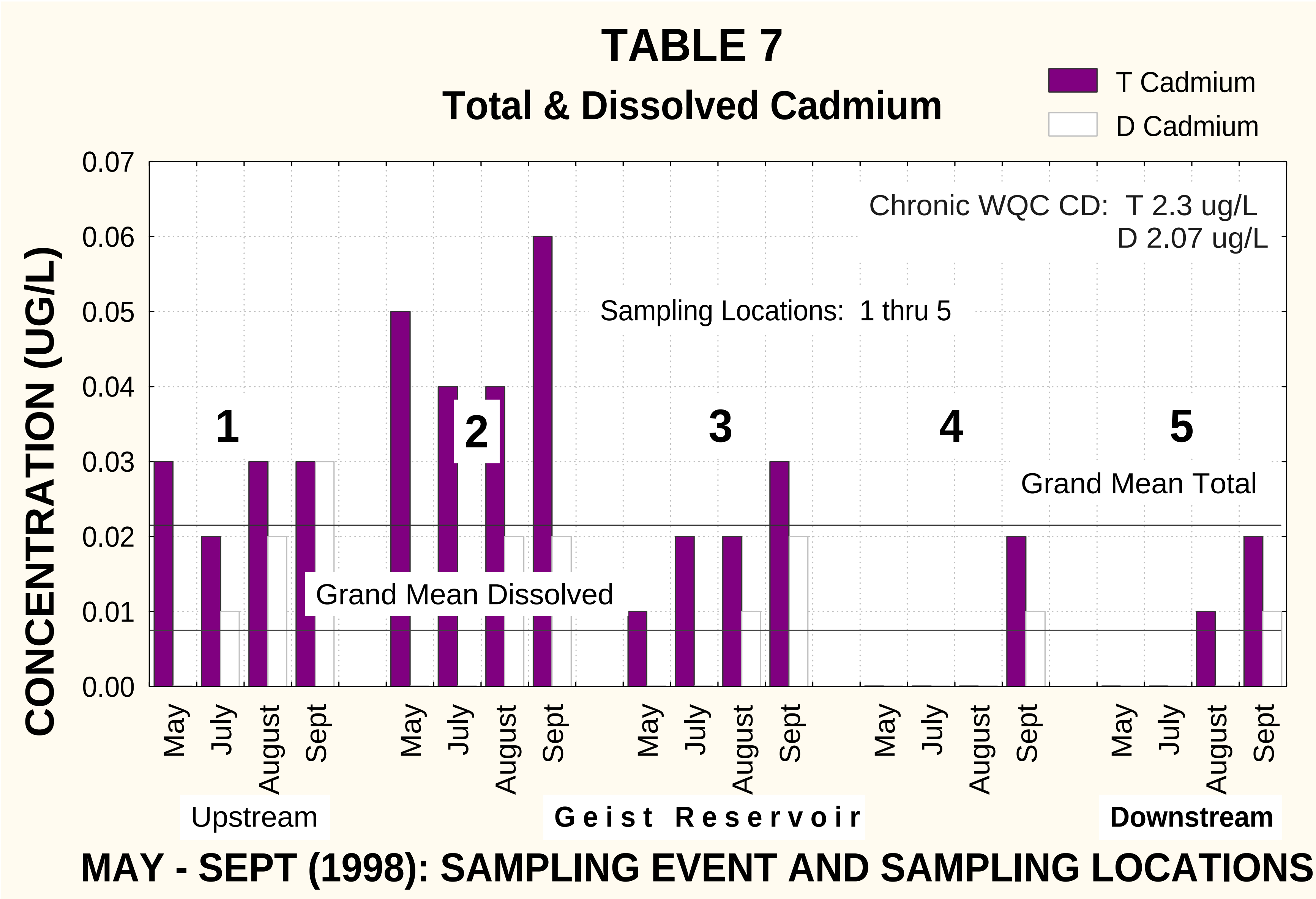


TABLE 7
Total & Dissolved Cadmium
T Cadmium
D Cadmium
CONCENTRATION (UG/L)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Chronic WQC CD: T 2.3 ug/L
D 2.07 ug/L
Sampling Locations: 1 thru 5
1
2
3
4
5
Grand Mean Total
Grand Mean Dissolved
May
July
August
Sept
Upstream
Geist Reservoir
Downstream
MAY - SEPT (1998): SAMPLING EVENT AND SAMPLING LOCATIONS

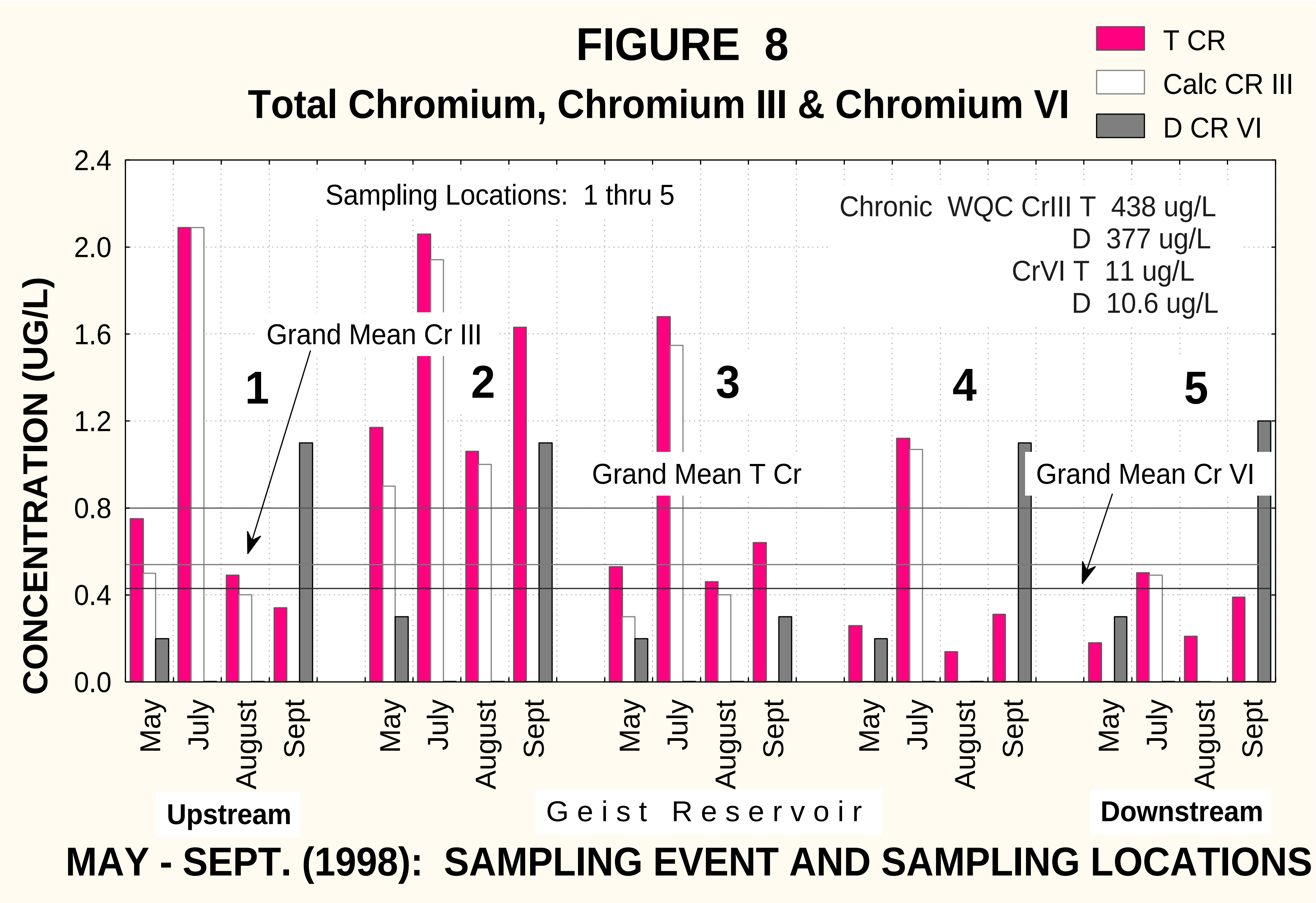


FIGURE 8
Total Chromium, Chromium III & Chromium VI
T CR
Calc CR III
D CR VI
Sampling Locations: 1 thru 5
Chronic WQC CrIII T 438 ug/L
D 377 ug/L
CrVI T 11 ug/L
D 10.6 ug/L
Grand Mean Cr III
Grand Mean T Cr
Grand Mean Cr VI
1
2
3
4
5
CONCENTRATION (UG/L)
2.4
2.0
1.6
1.2
0.8
0.4
0.0
May
July
August
Sept
Upstream
Geist Reservoir
Downstream
MAY - SEPT. (1998): SAMPLING EVENT AND SAMPLING LOCATIONS

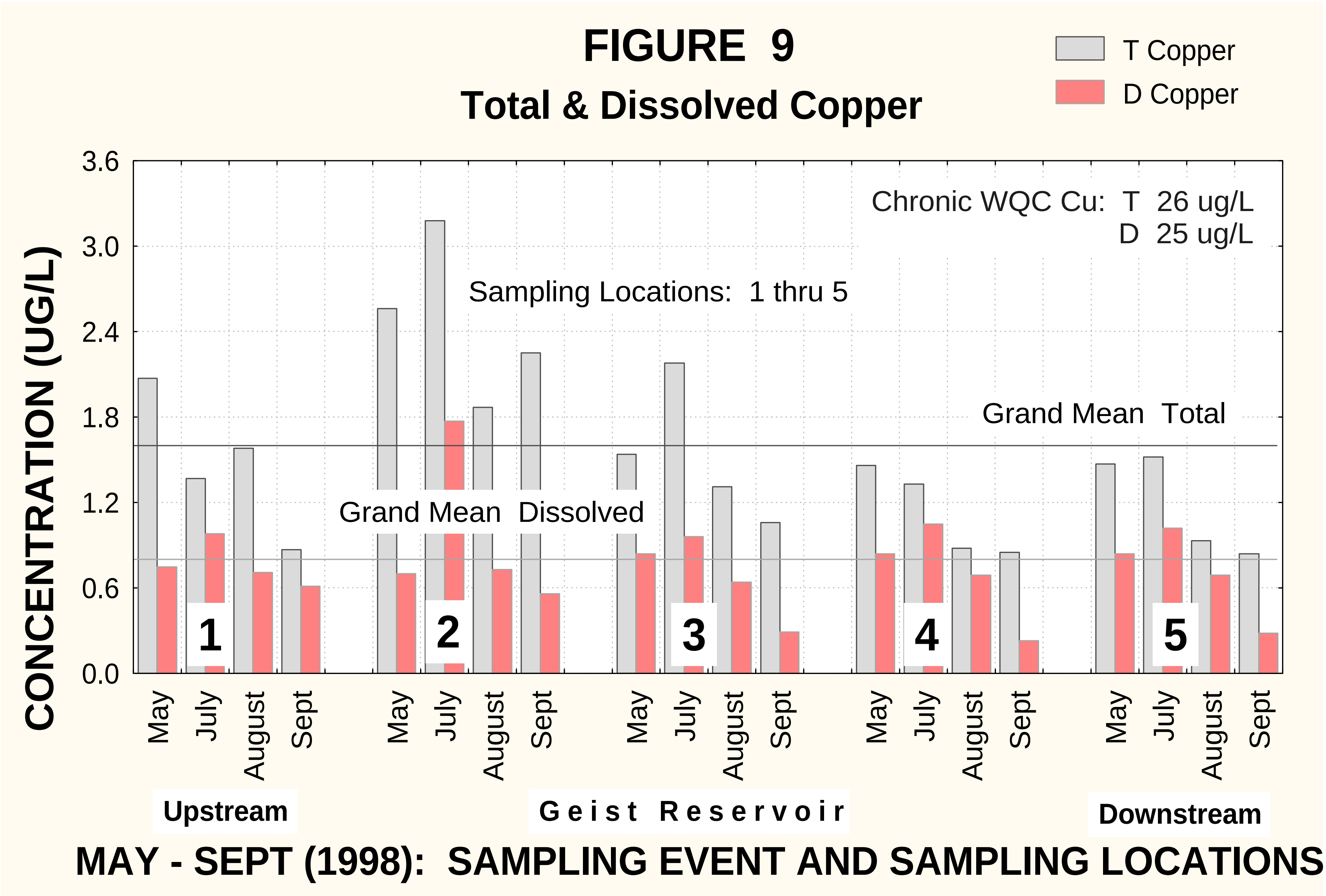


FIGURE 9
Total & Dissolved Copper
T Copper
D Copper
CONCENTRATION (UG/L)
3.6
3.0
2.4
1.8
1.2
0.6
0.0
Chronic WQC Cu: T 26 ug/L
D 25 ug/L
Sampling Locations: 1 thru 5
Grand Mean Total
Grand Mean Dissolved
1
2
3
4
5
May
July
August
Sept
Upstream
G e i s t R e s e r v o i r
Downstream
MAY - SEPT (1998): SAMPLING EVENT AND SAMPLING LOCATIONS

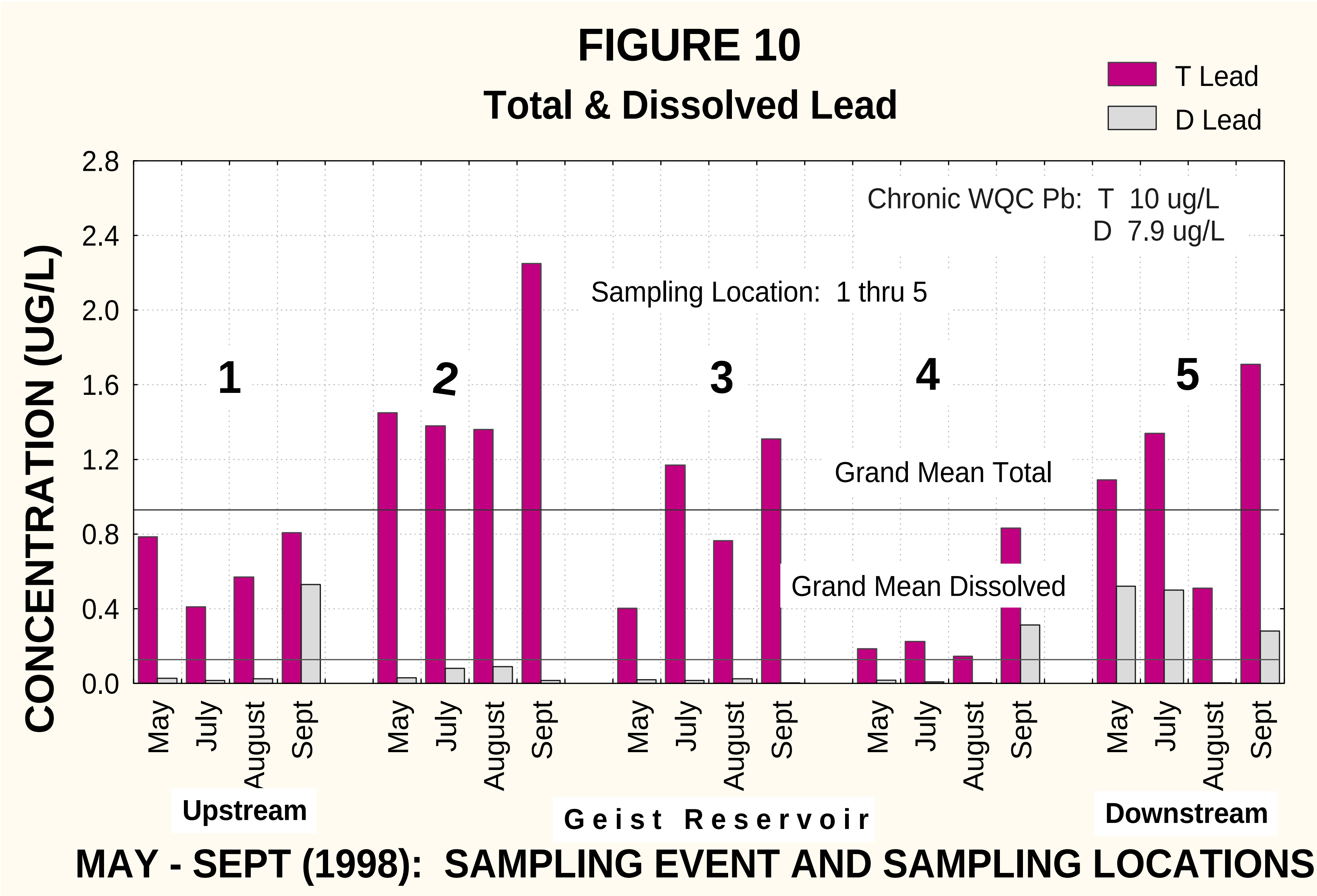


FIGURE 10
Total & Dissolved Lead
T Lead
D Lead
Chronic WQC Pb: T 10 ug/L
D 7.9 ug/L
Sampling Location: 1 thru 5
1
2
3
4
5
Grand Mean Total
Grand Mean Dissolved
CONCENTRATION (UG/L)
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
May
July
August
Sept
Upstream
Geist Reservoir
Downstream
MAY - SEPT (1998): SAMPLING EVENT AND SAMPLING LOCATIONS

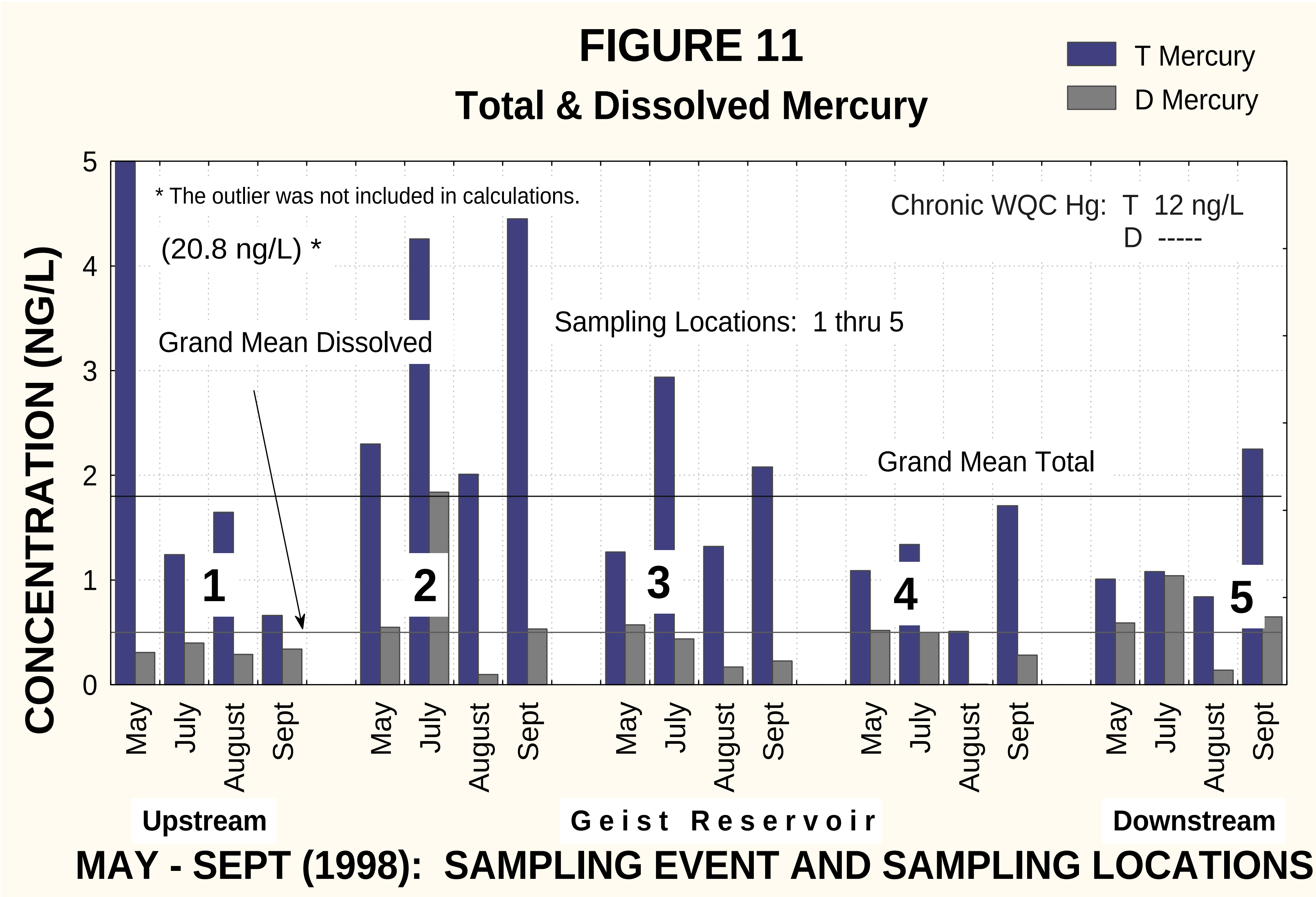
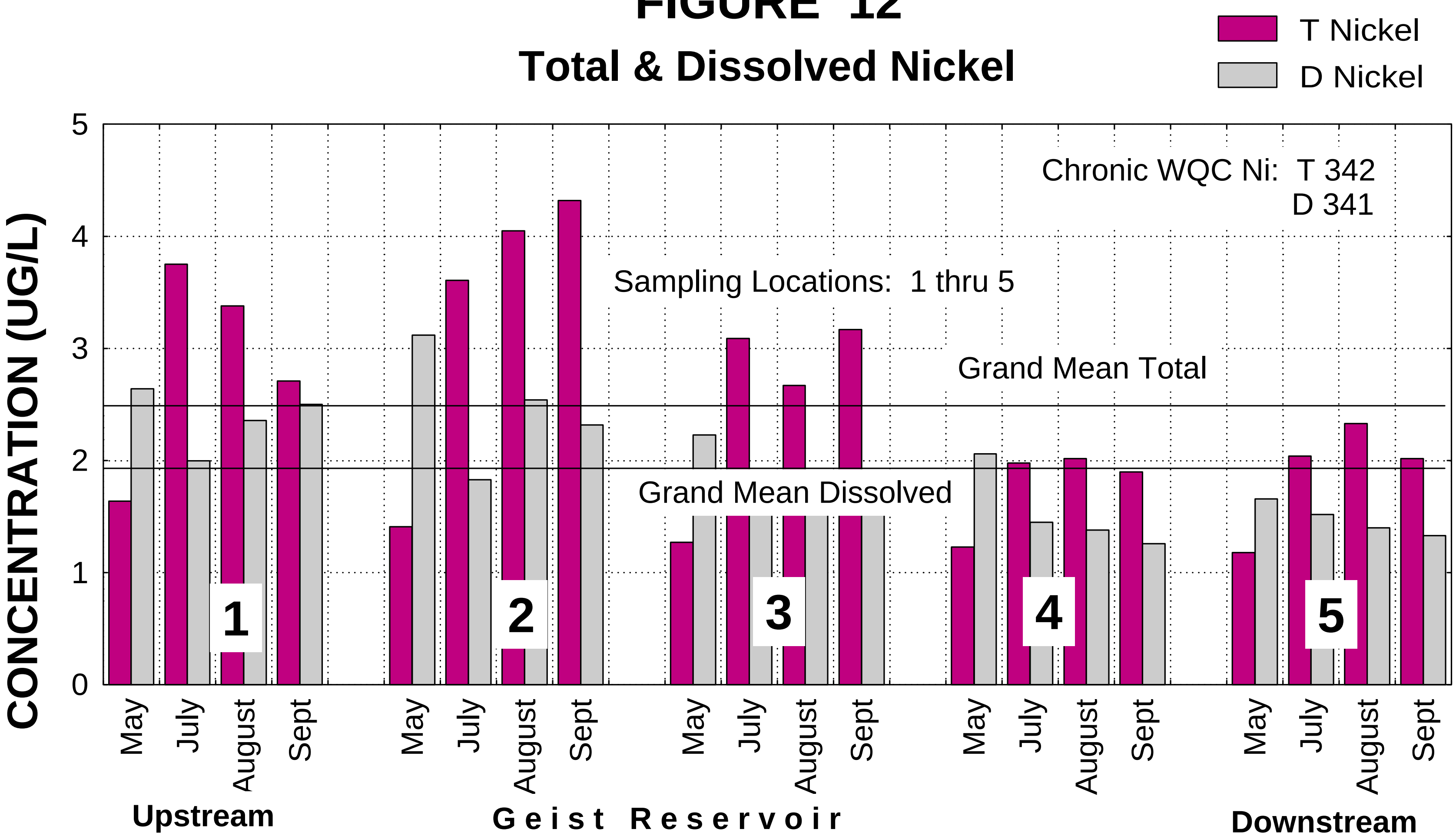


FIGURE 11
Total & Dissolved Mercury
T Mercury
D Mercury
* The outlier was not included in calculations.
(20.8 ng/L) *
Chronic WQC Hg: T 12 ng/L
D -----
Sampling Locations: 1 thru 5
Grand Mean Dissolved
Grand Mean Total
CONCENTRATION (NG/L)
0
1
2
3
4
5
1
2
3
4
5
May
July
August
Sept
Upstream
Geist Reservoir
Downstream
MAY - SEPT (1998): SAMPLING EVENT AND SAMPLING LOCATIONS

FIGURE 12

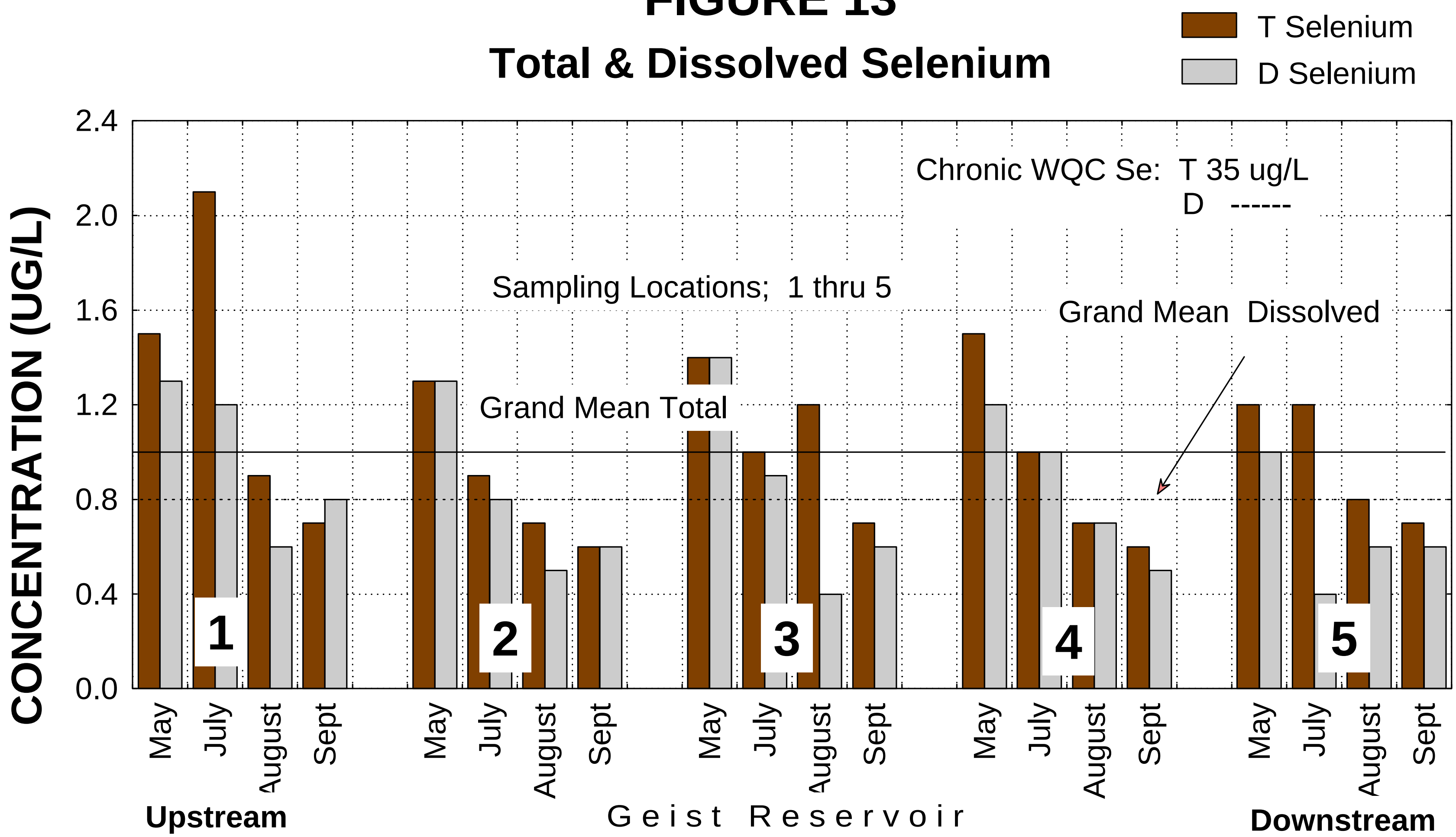
Total & Dissolved Nickel



MAY - SEPT. (1998): SAMPLING EVENT AND SAMPLING LOCATIONS

FIGURE 13

Total & Dissolved Selenium



MAY - SEPT (1998): SAMPLING EVENT AND SAMPLING LOCATIONS

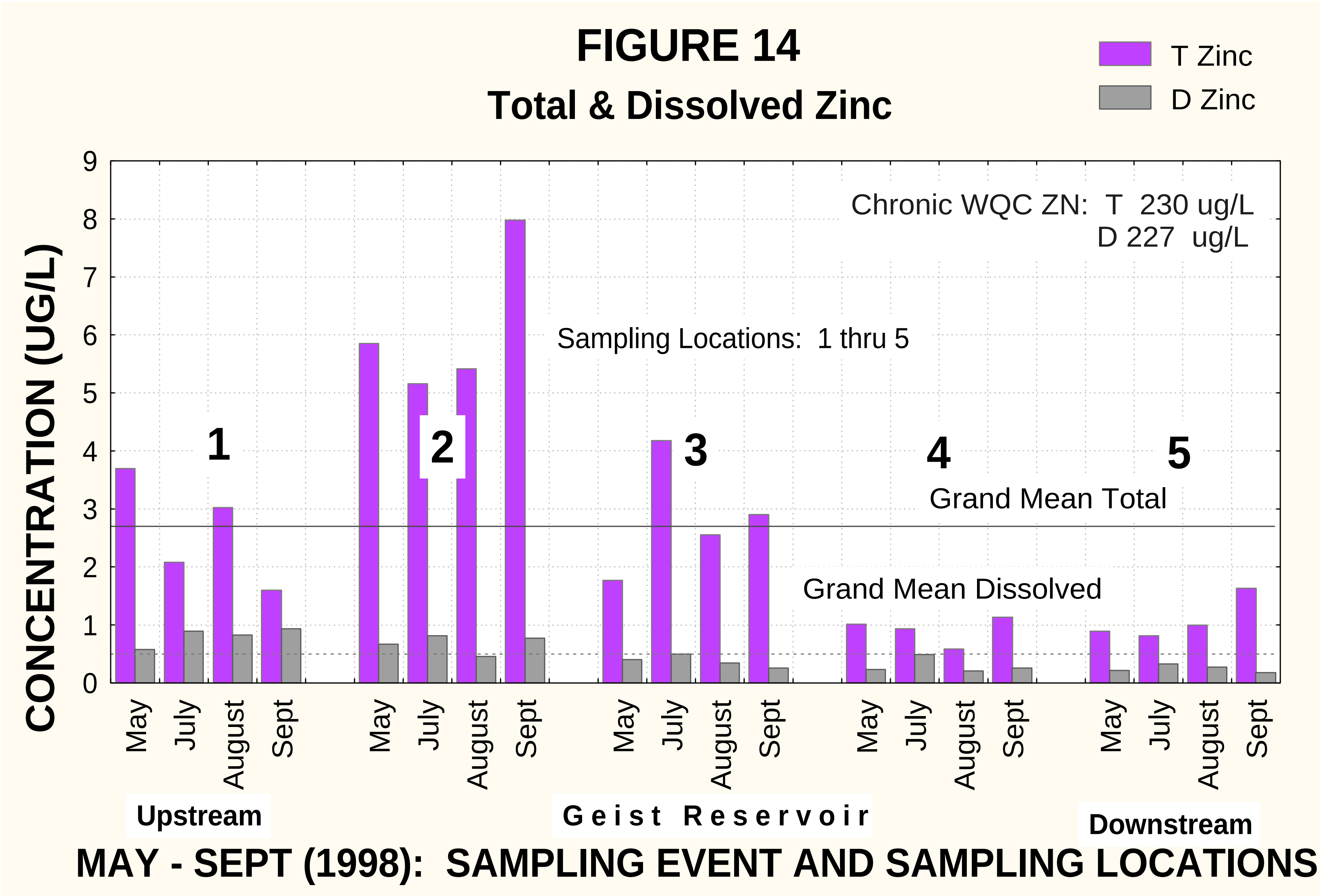


FIGURE 14
Total & Dissolved Zinc
T Zinc
D Zinc
CONCENTRATION (UG/L)
Chronic WQC ZN: T 230 ug/L
D 227 ug/L
Sampling Locations: 1 thru 5
1
2
3
4
5
Grand Mean Total
Grand Mean Dissolved
May
July
August
Sept
Upstream
G e i s t R e s e r v o i r
Downstream
MAY - SEPT (1998): SAMPLING EVENT AND SAMPLING LOCATIONS

assumptions for the true dissolved metal concentrations in the surface water. This evidently suggests that using low detect **Ultra-Clean** analytical test methods are very important and essential to analyze metals at trace levels, and use of **Clean Sampling Techniques** would be a complement to such analyses.

After the 1st and 2nd sampling event, because of inconvenience, several of the steps in "**Clean Sampling Techniques**" were left off or not followed strictly. This included not wearing the full overcoats, not covering the hands with long sleeve gloves, even not changing the wrist or elbow gloves frequently, or even covering the canopy using a plastic cover during sample collection. Because of such changes, analytical data for metals from sampling events 3 and 4 were not compromised and appeared to show no differences with the data obtained in the first two sampling events.

In fact, the Total Mercury concentration from the 1st sampling event at sampling location #1 (Upstream of Geist Reservoir) was about 10 times (**20.8 ng/L**) higher than all the other measurements made at other sampling locations (see **Table 3** & **Figure 11**) and also from all the other sampling locations from each sampling event. The **WSLH** reviewed all their bench record data for possible errors, but could not find any obvious reasons for such an error. The WSLH do recognize that in the 1st sampling event, there was an obvious in-lab Reagent Blank contamination problem. However, the WSLH does not believe that the **0.35 ng/L** mercury contamination in the in-lab Reagent Blank was high enough to indicate contamination of the water sample to 20.8 ng/L from the sampling location #1.

Contamination of other samples was non existent or minimal. Most of the metals or non-metals detected in the blanks were at or near Method Detection Limit (MDL) or the Limit of Quantitation (LOQ), except for nitrate and hexavalent chromium (Cr-VI). Nitrate was detected at 1.76 mg/L in the Field blank during the 3rd sampling event in August 1998. The WSLH attributes this to airborne contamination from opening nitric acid vial too close to nitrate sample aliquots. Similarly Cr-VI was detected at 1.3 ug/L in the tubing blank from September 1998 sampling event which was higher than the MDL and the actual sample value. The WSLH suspects this contamination may have occured during the preservation step or somewhere during the sample handling either in the field or laboratory. Since the dissolved Cr-VI concentrations were all lower, WSLH is confident that the contamination of the tubing blank did not occur during the filtering step.

In looking at all the metals and blank analyses data, it appears that IDEM staff did a good job in utilizing the "**Clean Sampling Techniques**" for the Trace Metal Pilot Project. However, as with any other sampling and analyses, a limited number of random contamination of field blanks was noticed but in no way does this appear to have compromised the actual total or dissolved metal concentration for a metal. As expected, in each and every sample from each sampling event, besides the total recoverable metals, dissolved metals were detected and their concentrations were always at or above the low detection limits for the individual metal. This certainly puts more weight and reasons for any future sampling and analyses for dissolved metals to use low detect sensitive test methods rather than the less sensitive conventional analytical method, where the concentrations of not only dissolved metals, but even the total metal concentrations often turn out to be below the detection limit (see **Table 8**).

CONCLUSIONS AND RECOMMENDATIONS

Conclusions:

A Trace Metal Pilot Project was undertaken to develop expertise in collecting ambient water samples using **"Clean Sampling Techniques"** and metal analyses by **Low Detect Ultra-Clean Analytical Test Methods.** The **Wisconsin State Laboratory of Hygiene** (**WSLH**) in Madison, WI was retained by IDEM as the Contract Analytical Lab for this pilot-project. **Fall Creek**, a point and a non-point source priority targeted watershed within the **White River Basin** was selected as the site for this Trace Metal Pilot Project.

- Training for sampling and collection of water samples using "**Clean Sampling Techniques**" was provided by personnel from WSLH (**Dr. Martin Shafer** & **Steve Hoffman**). **Dr Syed GhiasUddin**, **Steve Bosewell**, and **Betty Ratcliff** from IDEM participated in the first sampling event which also served as training for sampling surface water using the "Clean Sampling Techniques".

- The project required a minimum of 3 sampling events. IDEM staff completed 4 sampling events with near 100% completeness of target parameters tested.

- Several Problems at the Wisconsin Analytical Laboratory resulted in delay (Instrument breakdowns and moving labs) in performing analyses and obtaining results. These delays may have caused some minor errors in sample analysis and data reporting. The Final Analytical Data Report and in-lab data quality assessment was not completed by the Contract laboratory and sent to IDEM by July 13, 1999.

- Sampling by "**Clean Sampling Techniques**" is a very slow and laborious process requiring at least **3 staff members per site**, which is an increase of 1 full time staff predicted in preliminary planning. Each sampling event included 5 different sampling locations and took at least 3 days to complete 5 sampling locations for each sampling event.

- Based on experience gained from this study it is concluded that the "**Clean Sampling Technique**" for water samples collection on a large scale, such as for Fixed Station Monitoring Project or even a routine sampling of a watershed for water quality monitoring is **not feasible**. Perhaps, sampling on a limited basis for only a few parameters for a small water body with a very limited number of sampling locations would be possible.

- All the dissolved and total recoverable metal data collected for this pilot project appears to be of good quality because all the parameters were successfully measured at the low level detection limits. (See **Tables 3 to 6**). However, it is interesting to state that, except for Aluminum, none of the metal parameters in the Fall Creek exceeded the WQS (See **Table 8** and **Figures 5-14**).

- Results comparison obtained by using Traditional Sampling & Analytical methods from Fixed

Station in Fall Creek and those obtained using Clean Sampling Techniques and Ultra-Clean analytical methods could be made on total metals only and not dissolved. **Table 8** contains metals data from a Fixed Station Site (FC 0.6) downstream of Sampling Location # 5 (see **Figure 1**). As expected the traditional quantitation reporting limits were too high for most of the parameters to identify the real metal concentrations. From Fixed Station site the total metal concentrations for **Cadmium, Chromium, Copper, Lead, Mercury, Nickel,** and **Zinc** were approximately 5 to 10 times higher than the concentrations for the same metals obtained in this Pilot Project by using the Ultra-Clean Techniques for Sampling and Analysis. The difference between the Fixed Station metal data and those obtained in this study could be due to differences in sampling and analyses of ambient waters.

Recommendations:

- The **EPA Method 1669**, "Clean Sampling Techniques" is primarily developed to support the implementation of water quality at EPA water quality criteria (WQC) levels. This method is especially suitable for sampling and analyzing ambient waters for metals for which WQC are below the detection limit (**Antimony, Cadmium, Copper, Lead, Mercury, Nickel, Silver, Thallium, and Zinc**). The "Clean Sampling Technique" is also more valuable for collection and filtration of ambient water and subsequent determination of total and dissolved metals, instead of conventional test methods, by using low detect sensitive test methods to obtain results at the trace levels in the low parts per trillion (ppt or nanogram/L).

- The "**Clean Sampling Technique**" and low detect test methods are not intended for determination of metals at concentrations normally found in treated and untreated discharges from industrial or municipal facilities because existing regulations (**40 CFR Part 400-500**) typically limit concentrations of metals in the mid to high parts per billion range (ppb or ug/L). Therefore, use of these methods for analysis of metals in wastewater could be useful but are not essential for reporting compliance to the permit limits for metals.

- The **Method 1669**, "**Clean Sampling Techniques**" and the **Low Detect Ultra-Clean Analytical Test Methods**, because of complexities and being very slow and labor intensive, and also because of lack of many analytical labs to run the low detect ICP/MS analytical test methods, are not feasible and are not readily recommended for routine and large scale sampling and analysis of ambient waters for purposes of water quality monitoring. In lieu of this, conventional methods for sampling waters accompanied with low detect ICP/MS analytical methods could be a good substitute on a limited basis for small projects or even for large projects to monitor water quality for certain metals (**Antimony, Cadmium, Copper, Lead, Mercury, Nickel, Silver, Thallium**) for which the WQC are below the detection limits by conventional Graphite Furnace Atomic Absorption (GFAA) or Inductively Coupled Plasma (ICP) test methods.

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The training and expertise in clean sampling provided by the **Contact Laboratory-Wisconsin State Laboratory of Hygiene** (**WSLH**) at the University of Wisconsin, Madison, WI, to IDEM staff for this pilot project is greatly appreciated.

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APPENDIX A

SCOPE OF WORK

TRACE METALS PILOT PROJECT

Scope of Work

The Indiana Department of Environmental Management/ Office of Water Management (IDEM/OWM) requests proposals for contractual services to perform analysis of dissolved and total recoverable trace metals in surface waters in support of a pilot project to develop in-house ultra-clean low level trace metals collection expertise and capability. Contractual services are required to perform three support functions for the pilot project. Analysis of both the dissolved fraction and total sample of surface water stream samples for trace metals at ng/l levels and associated water quality parameters is required. Cleaning and preparation of sample bottles, sampling devices, and shipping materials for reuse is also required. Expert advice and assistance on ultra-clean trace metals sampling techniques and field procedures is desired.

Time frame: Sampling is planned to begin in the late spring or early summer of 1997. It is estimated that about 50 to 60 samples, including field QC samples, will be collected in three or four sampling events through mid summer 1998. The final laboratory report is tentatively planned for receipt at IDEM/OWM by August 1, 1998.

Mandatory Requirements

- **Analytical parameters and facilities:** Laboratory facility and instrumental equipment capable of analyzing dissolved and total water samples at ng/l levels of the following metals is required: aluminum, arsenic III, arsenic V, cadmium, chromium III, chromium VI, copper, iron, lead, manganese, mercury, nickel, selenium, silver, zinc. USEPA test methods for low level metals are required. USEPA methods 1631 through 1640 are suggested, but because this is a pilot project the bidder is encouraged to propose using test methods which will provide results at ng/l concentrations. It is anticipated that inductively couple plasma-mass spectroscopy (ICP-MS) methods will provide the lowest method detection and quantification limits for most of the target metals. Since the purpose of the analysis is to determine the quantity of dissolved metals at very low trace amounts, greater consideration will be given to proposals which provide the lowest detection and quantification limits. Results of method detection limit studies and guaranteed reporting quantification levels are required.

  Analysis of the following associated water quality parameters is requested: calcium, magnesium, sodium, potassium, sulfate, chloride, nitrate (or nitrate + nitrite), alkalinity, hardness, organic carbon, Kjeldahl nitrogen, phosphorus.

Samples for dissolved metals, anions (sulfate, chloride, nitrate), alkalinity, hardness, and nutrients (organic carbon, Kjeldahl nitrogen, phosphorus) will be filtered in the field through a 0.45 micron filter by OWM staff. Total recoverable metals and other parameters will be preserved if required in the field by OWM staff.

- **Experience:** A minimum of two years experience analyzing surface water samples for dissolved and total recoverable metals using USEPA trace metals clean room techniques in a facility which meets or exceeds the USEPA trace metals clean room requirements (sometimes referred to as "class 100 clean room") is required.[1]

- **Bottle preparation and sample shipping:** Cleaning, preparation and return of sampling devices, bottles, shipping containers, and any other equipment required for the next sampling event is required. A minimum of two years experience cleaning and preparing sampling equipment successfully is required. The laboratory will be required to clean and prepare sample bottles for reuse to collect samples. The laboratory will be expected to prepare a "kit" appropriately packaged with bottles and any other required equipment or consumables for shipment to IDEM/OWM in Indianapolis, IN for use before each scheduled sampling event. The trace metals "kit" includes shipping containers (coolers required) and refrigerant (blue ice), ready for use in the next sampling event. The proposer must make arrangements for shipping services for next day delivery of samples (with refrigerant) in one or two 32 quart coolers (or other appropriate size you would recommend) to the lab. Shipping costs must be included in the per sample cost. Coolers with bottles and freezer packs will be returned by the lab to IDEM/OWM for the next sampling event. Note: At this time IDEM/OWM plans to purchase sample bottles and use disposable filters and tubing. Indicate if bottles are included in your proposal, or if you have specifications which IDEM should use to procure bottles.

- **Field QC standards:** Field standards for chromium III extraction and field blanks at a frequency to be determined at the time of contract award are required. Proposals should include any other field check samples which the laboratory would recommend.

- **Quality Assurance Plan:** The laboratory is required to have a Quality Assurance Plan which meets USEPA Region 5 requirements or to endorse and follow the Quality Assurance Project Plan which OWM will write for this Trace Metals Pilot Project.[2] Quality assurance plans and quality control procedures must meet USEPA guidance for trace metals data

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[1] "Guidance on Establishing Trace Metal Clean Rooms in Existing Facilities", USEPA Office of Water, EPA 821-B-95-001, Draft, April 1995.

[2] "Content Requirements for Quality Assurance Project Plans for Water Division Programs," USEPA Region 5, QA Section, Revision 0, August 1994.

collection.[3] Performance of all QA and QC steps described in the methods is required. Describe the field and laboratory QC check samples which will be analyzed to meet requirements for the precision and accuracy of the methods being used. Proposals must include method detection limit, reporting limit (quantification limit), acceptance criteria, and precision and accuracy control limits.

- **Reporting and Deliverables:** IDEM/OWM maintains electronic databases of water quality results in addition to hard copy files of results and quality control data for each set of samples. Describe your capabilities to provide hard copy results, electronic report files in ASCII, dBase, or Paradox, the results of all QC check samples including duplicates, spikes, internal standards, field standards, field blanks, etc., and equipment calibration result details. Indicate what you will provide in your report for each set of samples submitted.

  Since the purpose of the project is to develop field methods, reported results will need to be received and reviewed before the next sampling event is scheduled. Reporting time of 30 days after the laboratory sample receipt date is requested. Proposals must indicate the report and sampling equipment turnaround time that can be supported.

- **Pricing:** Trace metals included in the proposed Indiana Water Quality Standards for the Lake Michigan Basin are included in the "Analytical parameters and facilities" paragraph. IDEM/OWM is interested in receiving the most cost effective results for metals which are analyzed by instrumental techniques as a group. Therefore, analysis of groups of metals which decreases the cost per element is encouraged. Instrumental methods such as ICP-MS which will report several elements at the same time in addition to the metals listed are most desirable.

  Provide the cost per sample for analysis of dissolved and total recoverable metals including blanks, matrix spikes, and any other QC check sample you recommend. Indicate if charges are itemized or inclusive for sample bottle cleaning, "kit" return, sample preparation, and analysis. Indicate if charges are per sample batch or a separate charge per sample. Also include the cost per sample for the associated water quality parameters. IDEM must be able to determine cost per sample for evaluation purposes.

  The IDEM/OWM anticipates purchasing sample bottles and USGS type field water sampler for use in wadeable streams. Proposals may include suggestions for sample bottle types or comments on sample volume needs. Include sample device price if you intend to supply a sampling device.

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[3] "Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring," USEPA Office of Water Engineering and Analysis Division, Washington D.C., EPA 821-B-95-002, April 1995.

Desirable Requirements

- Assistance in developing sampling expertise is desired. Demonstrated field expertise in the handling, use, and cleanup of sampling equipment for collection of ultra-clean trace metals samples is desired. Capability to provide expert advice and assistance in using sampling devices suitable for collecting dissolved water samples filtered in the field and total water samples to meet the requirements of USEPA sampling method 1669 is desired.[4]

- A sampling device for use in wadeable streams to collect depth and width integrated samples is needed by OWM. Describe in your proposal the sampling device you will supply. Provide expert assistance if required for development of field sampling techniques and training. Describe your experience and expertise in ultra-clean trace metals sampling including company history, personnel expertise, sampling equipment used, and willingness to travel to Indiana if required.

Proposals

Proposals must include the following information to be considered for contract award.

- Itemized description of laboratory equipment and facilities which will be used to analyze the samples and cleanup bottles and field equipment for use in the next sampling event.

- Description of staff experience and expertise in laboratory analysis and field sampling expertise.

- Quality Assurance Project Plan for the laboratory which is used for trace metals analysis projects. Describe the QC steps and QA procedures which are included in the trace metals analysis program.

- Description of and list of QC check samples which will be used to provide quality control for results. Include laboratory and field QC samples. Describe and identify precision and accuracy acceptance criteria and control limits for both field and laboratory QC samples for each parameter.

- Include method detection limit study as described in 40CFR Part 136 Appendix B for each parameter. Indicate your lowest reporting limit (quantification limit) for each parameter.

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[4] "Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels", USEPA Office of Water Engineering and Analysis Division, Washington, DC, EPA 821-R-95034, April 1995.

- Provide an example report which includes all of the requested information identified above and any additional information which your laboratory normally reports or which is appropriate or necessary for the interpretation of the analytical parameters requested.

- Describe the turnaround time from sample receipt at your laboratory until report receipt by OWM. Indicate the bottle cleaning and preparation turnaround time from date of sample receipt at your laboratory until recycled field kit receipt by OWM.

- Describe your capabilities to clean and prepare sample bottles and associated consumable supplies for ultra-clean trace metals sampling. Provide any recommendations you have for filters and tubing as far as one-time use versus reuse. Describe how you will package and what you will include in a sampling "kit" to collect an ultra-clean trace metals sample.

- Provide cost per sample for analysis of groups of metals. Indicate if bottle cleanup and preparation is included or priced separately. Provide cost per sample for other parameters. Provide cleanup and bottle preparation costs separately for associated water quality parameters. Bottles may not be reused, or clean bottle preparation may not be necessary.

- Describe how your lab would assist and provide on site expertise for one sampling event.

- Describe in detail the metal free USGS type integrating sampler for wadeable streams you propose to provide and the cost. List the appropriate replaceable sample bottle sizes available for the sampler and the cost per bottle for each size bottle.

- Provide telephone number and address of one to three references of customers, for whom you have performed low level trace metals analysis, which IDEM can contact.

Proposal Evaluation

Proposals will be evaluated based upon the proven capability of the proposer to satisfy mandatory and desirable requirements of this Scope of Work cost effectively. All proposals will be reviewed by IDEM/OWM staff.